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NASA Conference Publication 2235

# Applying Modeling Results in Designing a Global Tropospheric Experiment

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*Proceedings of a working group meeting  
held in Virginia Beach, Virginia  
July 15-16, 1981*

**NASA**

# Applying Modeling Results in Designing a Global Tropospheric Experiment

Proceedings of a working group meeting sponsored by  
the NASA Office of Space Science and Applications  
and Langley Research Center  
and held in Virginia Beach, Virginia  
July 15-16, 1981

**NASA**

National Aeronautics  
and Space Administration

**Scientific and Technical  
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## PREFACE

In formulating research efforts within the National Aeronautics and Space Administration's Tropospheric Air Quality Program, NASA has sought and utilized the advice of the scientific community. The NASA Working Group on Tropospheric Program Planning, led by Dr. John Seinfeld, established a foundation to guide program development (NASA RP-1062, 1981). Additional planning activities are being conducted in order to identify specific research tasks. One such planning effort was conducted by the Working Group on the Application of Modeling Research Results to the Design of a Global Tropospheric Experiment, which met in Virginia Beach, Virginia, July 15-16, 1981. The objectives of this working group were: (1) to determine the extent to which existing models can guide the design of global tropospheric field experiments, and (2) to identify near-term modeling research problems which, if resolved, would enhance the design of sampling strategies for future measurement opportunities.

As this program continues it must address the pertinent scientific issues of the trace constituents within the troposphere on a truly global scale. Much research is still required, and we look to efforts such as these to provide meaningful guidance. The assistance of all those who contributed to this working group is sincerely appreciated.

Robert J. McNeal, Manager  
Tropospheric Air Quality Program  
Office of Space Science and Applications

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## CONTENTS

<u>PREFACE</u> . . . . .	
<u>EXECUTIVE SUMMARY</u> . . . . .	1
<u>INTRODUCTION</u> . . . . .	3
<u>OBJECTIVES AND ORGANIZATION</u> . . . . .	4
<u>SOURCES, SINKS, AND BOUNDARY LAYER INPUT TO THE FREE TROPOSPHERE</u> . . . . .	5
<u>TROPOSPHERIC OZONE CYCLE</u> . . . . .	5
Scientific Background and Issues . . . . .	5
Proposed Field Measurements . . . . .	8
<u>TROPOSPHERIC CARBON CYCLE</u> . . . . .	9
Methane . . . . .	9
<u>Scientific Background and Issues</u> . . . . .	9
<u>Proposed Field Measurements</u> . . . . .	11
Carbon Monoxide . . . . .	13
<u>Scientific Background and Issues</u> . . . . .	13
<u>Proposed Field Measurements</u> . . . . .	15
Nonmethane Hydrocarbons . . . . .	15
<u>Scientific Background and Issues</u> . . . . .	15
<u>Proposed Field Measurements</u> . . . . .	16
<u>TROPOSPHERIC NITROGEN CYCLE</u> . . . . .	17
Scientific Background and Issues . . . . .	17
Proposed Field Measurements . . . . .	18
<u>TRACE METALS</u> . . . . .	21
Scientific Background and Issues . . . . .	21
Proposed Field Measurements . . . . .	22
<u>TROPOSPHERIC SULFUR CYCLE</u> . . . . .	23
Scientific Background and Issues . . . . .	23

<u>Distribution and Sources of Sulfur Species</u> . . . . .	23
<u>Homogeneous Chemistry</u> . . . . .	24
<u>Heterogeneous Removal</u> . . . . .	25
<u>Dry Deposition</u> . . . . .	26
Proposed Field Measurements . . . . .	26
MODELING RESEARCH TO SUPPORT SOURCE-SINK STUDIES AND BOUNDARY LAYER INFLUENCE ON THE FREE TROPOSPHERE . . . . .	27
Multicycle and Multidimensional Models . . . . .	27
Roles for One-Dimensional Photochemical Modeling . . . . .	28
<u>STRATOSPHERIC-TROPOSPHERIC EXCHANGE</u> . . . . .	31
INTRODUCTION . . . . .	31
Chemicals Significantly Affected by Stratospheric-Tropospheric Exchange . . . . .	31
Transport . . . . .	35
PROPOSED FIELD MEASUREMENTS . . . . .	36
Measurement Programs . . . . .	36
Regions of the Atmosphere in Which Measurements Would Be Conducted . . . .	37
PROPOSED MODELING RESEARCH . . . . .	38
<u>FAST PHOTOCHEMICAL PROCESSES IN THE FREE TROPOSPHERE</u> . . . . .	39
PROPOSED MODELING RESEARCH . . . . .	39
Fast Photochemical Models . . . . .	39
Regional-Scale Models . . . . .	40
Heterogeneous Processes . . . . .	41
Development of Diagnostic and Prognostic Global Models . . . . .	42
Development of 3-D Global Models . . . . .	42
PROPOSED FIELD MEASUREMENTS . . . . .	43
Fast Photochemistry of OH . . . . .	45
Fast Photochemistry of HO <sub>2</sub> . . . . .	46

# BEST DOCUMENT AVAILABLE

Fast Photochemistry of $\text{CH}_3\text{O}_2$ . . . . .	47
$\text{NO}_2/\text{NO}$ Photostationary State . . . . .	48
$\text{NO}_y$ Partitioning . . . . .	49
Fast Photochemistry of Sulfur . . . . .	50
Fast Photochemistry of Halogen Species . . . . .	53
<u>LONG-TERM MONITORING TO UNDERSTAND TROPOSPHERIC VARIABILITY</u> . . . . .	56
SCIENTIFIC BACKGROUND AND ISSUES . . . . .	56
PROPOSED RESEARCH . . . . .	57
<u>APPENDIX A - ATTENDEES</u> . . . . .	59
<u>APPENDIX B - MODELING STUDIES CURRENTLY SUPPORTED BY NASA</u> <u>TROPOSPHERIC AIR QUALITY PROGRAM</u> . . . . .	60
<u>APPENDIX C - POTENTIAL TEMPERATURE AND POTENTIAL VORTICITY</u> Edwin F. Danielsen . . . . .	69
<u>REFERENCES</u> . . . . .	76

## EXECUTIVE SUMMARY

This document reports the recommendations of the NASA Working Group on the Application of Modeling Research Results to the Design of a Global Tropospheric Experiment. These recommendations evolved through an exchange of written materials both before and after the working group meeting, which was held July 15-16, 1981.

The working group identified a set of field experiments and advanced modeling studies which provide a strategy for a program of global tropospheric experiments. The principal recommendations in this document can be summarized as follows:

1. The chemical species most critical to advancing the understanding of homogeneous gas-phase chemistry of the troposphere include OH, NO, and NO<sub>2</sub>. Techniques for measurement of these species in nonurban, remote atmospheres are under development, but have not yet demonstrated satisfactory accuracy or precision. Completion of instrument research, development, and testing for measurement of OH, NO, and NO<sub>2</sub> in the remote troposphere is a top-priority activity.

2. There is a second group of gaseous chemical species, including CO, O<sub>3</sub>, halogens, certain trace metals, and reduced sulfur species, for which it is possible to make accurate, precise measurements both on the ground and from aircraft. The climatology of the global distribution of these species needs to be established. Any field program should include both ground measurements and atmospheric profiles of these species. Data on seasonal variability at specific sites and interhemispheric gradients are of particular importance.

3. Working-group members concerned with measurements in the boundary layer placed strong emphasis on the need to develop capabilities for direct measurement of chemical flux between Earth surface sources and sinks, the boundary layer, and the free troposphere. Techniques are described for meteorological and ozone flux measurements from aircraft. A recommendation that additional fast-response chemical sensors be developed to increase capabilities for airborne flux measurements is made, with emphasis on particular needs for flux data on O<sub>3</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, NMHC, and gaseous reduced sulfur species over oceans, tropical forests, wetlands, and areas of biomass burning.

4. In order to quantify global tropospheric budgets of chemical species such as O<sub>3</sub>, NO, NO<sub>2</sub>, and H<sub>2</sub>O, exchange between the troposphere and stratosphere must be investigated in detail. The working group on stratosphere-troposphere exchange recommends a program of field measurements in midlatitude tropopause fold structures; these are regions of active stratosphere-troposphere exchange and large chemical gradients. Meteorological techniques using potential vorticity can be used to guide aircraft chemical sampling and to extrapolate results to global flux. A second region of particular importance for assessing troposphere-stratosphere exchange is the Intertropical Convergence Zone, where high altitude cumulus towers penetrate the tropopause.

5. In the area of modeling research needs for global tropospheric studies, the working group stressed the need for emphasis on the development of coupled dynamic-photochemical models to explore the global budgets of O<sub>3</sub>, CO, and other critical chemical species. One-dimensional and two-dimensional models will continue to play a critical role in regional transport and geochemical budget studies and also in exploring new chemical reaction schemes.



6. Longer-range goals for a global tropospheric research program must include understanding the role of complex heterogeneous processes in global budgets. The working group recognized that while extensive research is currently in progress on regional air pollution chemistry, studies of heterogeneous processes in remote, non-urban tropospheric regions are in the very early stages of development. In the next few years particular emphasis must be placed on the development of both collection and analytical techniques for ground and airborne measurements of gas-particle reactions, precipitation scavenging processes, and chemical deposition in oceanic and remote continental regions.

7. An area of laboratory research which is of particular importance to support many of the proposed modeling and field studies concerns the production and atmospheric reactivity of nonmethane hydrocarbon species by tropical vegetation.

8. The working group stressed the importance of careful research into and monitoring of long-term trends in long-lived tropospheric trace gases such as  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and certain halocarbon species. It was felt that NASA should explore the potentially unique role for application of space technology to long-term monitoring of the global troposphere.

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## INTRODUCTION

As part of its continuing efforts to direct its applications programs toward relevant national needs, NASA is conducting a Tropospheric Air Quality Program, the long-range objective of which is to apply NASA's space technology to assess and predict human impact on the troposphere, particularly on the regional to global scale. The synoptic view afforded by satellites and the increasing importance of pollution on these scales suggest that space observations can play a unique and critical role in this endeavor. Because the large-scale troposphere is poorly understood at the present time, NASA recently sponsored a working group of scientists who prepared an overview of the scientific problems that need to be addressed in order to understand the regional and global troposphere (Seinfeld et al., 1981). The group recommended that NASA undertake an expanded effort to develop space applications for tropospheric air quality monitoring and studies. This would include instrument development, modeling, laboratory studies, and field measurement activities. Implementing these recommendations is currently the major thrust of NASA's Tropospheric Air Quality Program.

To help NASA in formulating a detailed implementation plan, assistance is sought from workers in this field to identify the high-priority research required in each of the four program components: instrument development, modeling, laboratory studies, and field measurements.

This volume reports the results of the Working Group on the Application of Modeling Research Results to the Design of a Global Tropospheric Experiment. This meeting was sponsored by the NASA Office of Space Science and Applications and conducted under the direction of Langley Research Center. The support of The Bionetics Corporation, and particularly the assistance of Howard J. Curfman, Jr., and Helen Ann Thompson, is gratefully acknowledged.

## OBJECTIVES AND ORGANIZATION

The objectives of the working group meeting were to pursue answers to the following questions:

- (1) What guidance do existing models offer for the design of a global tropospheric field experiment program? More specifically, what priorities should be established for measurement needs in global tropospheric research in the light of current chemical and dynamic understanding? What spatial and temporal scales of importance can be identified for the design of a sampling strategy to obtain data which will improve our understanding of large-scale tropospheric processes?
- (2) What are the near-term modeling research problems which, if resolved, will enhance the design of a tropospheric air sampling program?

The working group participants included atmospheric modelers currently sponsored by the NASA Tropospheric Air Quality Program as well as several researchers representing specialized areas. (See Appendix A for a listing of working group participants.) A summary of the modeling activities currently supported by this program is contained in Appendix B. In order to accomplish the objectives, the working group was organized into three task groups. The task group organization and membership are as follows:

Robert C. Harriss, Working Group Chairman

### Task Group on Sources, Sinks, and Boundary Layer Input to the Free Troposphere

Gregory R. Carmichael  
Ralph J. Cicerone  
Jack Fishman

Ronald J. Lantzy  
Donald H. Lenschow  
Leonard K. Peters

### Task Group on Stratospheric-Tropospheric Exchange

Edwin F. Danielsen  
James E. Hansen  
Shaw Liu

Richard S. Stolarski  
Owen B. Toon

### Task Group on Fast Photochemical Processes in the Free Troposphere

William L. Chameides  
Jennifer A. Logan

Michael B. McElroy  
Richard W. Stewart

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## SOURCES, SINKS, AND BOUNDARY LAYER INPUT TO THE FREE TROPOSPHERE

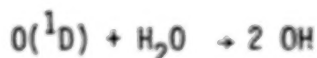
### TROPOSPHERIC OZONE CYCLE

#### Scientific Background and Issues

Developing an understanding of the tropospheric ozone cycle is a fundamental prerequisite for deriving an accurate picture of many of the other trace constituents in the troposphere. It is the presence and subsequent photolysis of ozone which initiates the production of the hydroxyl radical (Levy, 1971) in the natural troposphere:



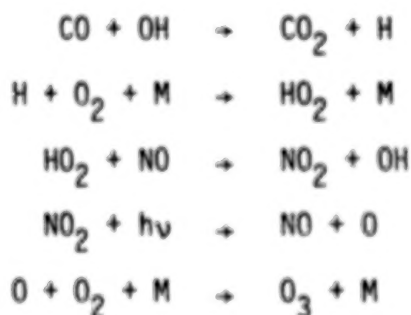
followed by:



In turn, OH-initiated reactions are responsible for the primary homogeneous loss mechanisms of many of the important trace gases in the carbon, nitrogen, and sulfur families of reactants. In addition, many other anthropogenic and naturally produced hydrocarbon and chlorinated compounds would build to much higher tropospheric concentrations if they were not removed through OH-initiated reactions.

The details of the tropospheric ozone cycle, shown in figure 1, are not well understood at the present time. Prior to 1970, it was generally assumed that ozone was an inert chemical species in the natural or unpolluted troposphere. Thus, all ozone found in the natural troposphere was assumed to originate in the stratosphere, and could therefore be used as a tracer of stratospheric injection (Danielsen and Mohnen, 1977). It was also assumed that ozone eventually was destroyed when it came into contact with land or water surfaces (Junge, 1962; Aldaz, 1969). This picture changed when it was shown that a considerable amount of OH (as well as other radicals and formaldehyde) should be produced in the natural troposphere, which would result in a significant photochemical sink for tropospheric ozone (Chameides and Walker, 1973; Crutzen, 1974).

The cycle is further complicated by the fact that there are chemical sequences initiated by OH which can result in *in situ* production of tropospheric ozone. The simplest and possibly the largest in magnitude of these reaction chains (Fishman et al., 1979b) is the oxidation of carbon monoxide (CO):



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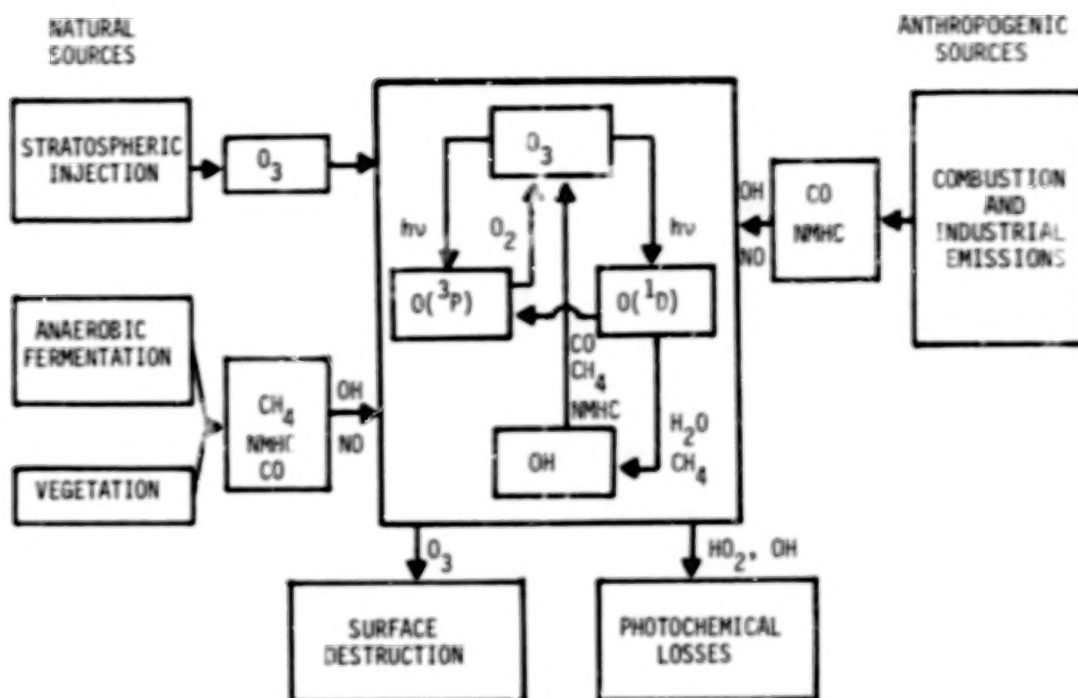
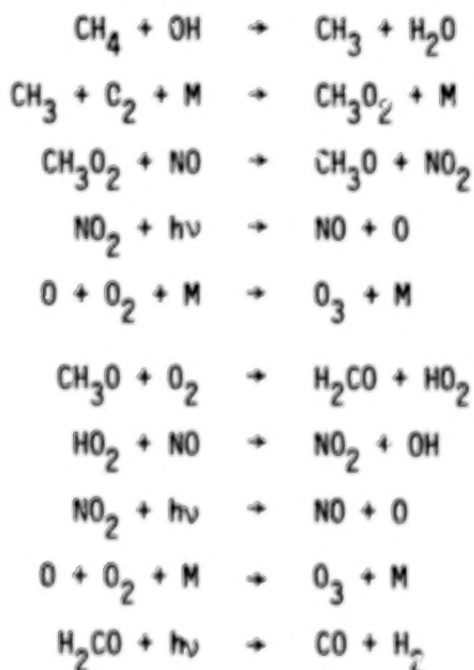


Figure 1. Tropospheric ozone cycle.

The *in situ* photochemical production of tropospheric ozone is also initiated by the oxidation of methane ( $CH_4$ ) by  $OH$ :





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Note that the methane oxidation chain, in addition to yielding ozone, also produces CO, which can eventually form additional ozone via the carbon monoxide oxidation chain. A similar and somewhat more complicated reaction sequence (Zimmerman et al., 1978) has been proposed for the nonmethane hydrocarbons (NMHC). The net products of all these reaction sequences result in the *in situ* production of tropospheric ozone if sufficient oxides of nitrogen ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) are present. However, current measurements of the distribution and background concentrations of  $\text{NO}_x$  in the troposphere vary considerably, which makes it difficult to determine whether photochemical processes serve as a net source or net sink of tropospheric ozone. Nonetheless, integration of the photochemical production and destruction rates of tropospheric ozone on the global scale indicates that these processes are comparable in magnitude to the amount of ozone transported through the tropopause or the amount destroyed at the Earth's surface.

The destruction rate at the Earth's surface can be determined using existing technology to measure the ozone deposition flux directly. A climatology for these deposition rates should be determined for various locations chosen to represent typical land and ocean surfaces around the world. Thus, it appears that a measurement program can be implemented to determine the contribution of these physical phenomena to the global tropospheric ozone cycle.

On the other hand, it is much more difficult to establish a measurement program to evaluate the magnitude of the photochemical production and destruction of ozone. In the remote troposphere, photochemical processes produce or destroy ozone at a rate of only a few parts per billion per day, which most likely could not be discerned directly through a measurement program. To resolve the uncertainty in the ozone cycle, it will be necessary to have concurrent measurements of ozone and other atmospheric trace gases such as CO,  $\text{NO}_x$ , or some hydrocarbons. A sound tropospheric photochemical modeling effort which includes the correct meteorological dynamics would be necessary to evaluate the meaning of such observations for the scale on which the measurements are made (e.g., mesoscale or regional scale).

Even if the *in situ* photochemical production rate of tropospheric ozone could be measured, it would still be difficult to determine what fraction of this ozone came about because of anthropogenic activity. Unlike other trace gases, ozone is not released directly into the atmosphere, and thus an emissions inventory cannot be attempted. A calculation of the percentage of tropospheric ozone resulting from human activity can be made only after the anthropogenic contribution to the release of CO, hydrocarbons, and  $\text{NO}_x$  is fairly well known. Thus, it is clear that an understanding of the tropospheric ozone cycle first requires a comprehensive knowledge of the cycles of other tropospheric trace gases.

The question of climate modification is likewise important when considering the global cycle of tropospheric ozone. Ozone is an optically active gas which absorbs and emits terrestrial infrared radiation in the 8- to 10- $\mu\text{m}$  region. Even though only about 10 percent of all ozone is found in the troposphere, a uniform percentage increase of ozone in this region has about the same net radiative heating effect on the lower troposphere as the same percentage increase of stratospheric ozone. The relatively strong sensitivity of the terrestrial radiative energy balance is primarily a result of the fact that the 9.6- $\mu\text{m}$  band opacity of ozone is a function of atmospheric pressure.

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Calculations indicate that a doubling of tropospheric ozone will result in an average hemispheric increase in temperature of about 1 K. Using the same climatic sensitivity parameters, a doubling of CO<sub>2</sub> would result in an increase of 2 to 3 K. The sparse data base presently available for tropospheric ozone indicates that there may be considerably more (25 to 50 percent) ozone in the Northern Hemisphere than in the Southern Hemisphere. Whether or not this hemispheric difference is a result of human activity is not definitely known at the present time. In any case, because ozone has a relatively short atmospheric residence time, most of the radiative effects would be concentrated in the Northern Hemisphere (where CO<sub>2</sub> would be uniformly mixed), producing an even more complicated picture of the possible perturbation to climate.

In summary, the research requirements for the global ozone cycle are:

1. Develop climatology of surface loss rate of ozone
2. Quantify the photochemical production and loss processes in the troposphere
3. Assess the impact of anthropogenic activity on the natural tropospheric ozone cycle

## *Proposed Field Measurements*

The implementation of the first research requirement is fairly straightforward and technically feasible at the present time. Fast-response ozone sensors can be employed to measure the ozone flux directly in the upper troposphere (using an aircraft platform), or at the Earth's surface (employing an instrumented tower). In addition, our understanding of the synoptic-scale processes influencing transport out of the stratosphere would be greatly enhanced if a three-dimensional distribution of ozone were available in the vicinity of tropopause folding events. The use of the UV-DIAL system flying beneath the tropopause fold in an upward-pointing mode should provide some illuminating data to study this phenomenon. Stratosphere-troposphere exchange is discussed in the next section of this document.

Although several research groups have looked at ozone destruction rates at various surfaces in recent years (e.g., Galbally and Roy, 1980; Wesely et al., 1981; Lenschow et al., 1981), knowledge of the global destruction rate is still limited. Galbally and Roy have made the most recent estimate of the global destruction rate of ozone at the Earth's surface, and have arrived at values of  $1.0 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $0.7 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$  for the Northern and Southern Hemisphere, respectively. This is consistent with the review presented by Gidel and Shapiro (1980) which gives ranges of  $0.7$  to  $1.1 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$  and  $0.4$  to  $0.6 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$  for the two hemispheres.

However, the more recent observations of Wesely et al. (1981) and Lenschow et al. (1981) suggest that Galbally and Roy's (1980) deposition velocity over water is 2 to 10 times too high. The distribution of ozone used by Galbally and Roy to compute hemispheric destruction rates is inconsistent with the recent measurements of



Routhier et al. (1980) and Seiler and Fishman (1981). Whereas Galbally and Roy tropospheric  $O_3$  distribution results in 15 to 20 percent more ozone in the Southern Hemisphere in the remote boundary layer, the data of Routhier et al. and Seiler and Fishman indicate about 50 percent more  $O_3$  in the Northern Hemisphere than in the Southern Hemisphere. Taking the above factors into account lowers the Southern Hemispheric estimate of Galbally and Roy from  $0.7$  to  $0.3-0.6 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$  and increases their Northern Hemispheric estimate from  $1.0$  to  $1.2-1.6 \times 10^{11} \text{ mol cm}^{-2} \text{ s}^{-1}$ . These modifications to the Galbally and Roy study greatly influence the ratio of the destruction rates between the Northern and Southern Hemispheres, which in turn has a large impact on the amount of *in situ* photochemical production necessary to derive a balanced global tropospheric ozone budget. Thus, even with these excellent studies completed in recent years, it is evident that this component of the tropospheric ozone budget still has not been quantified well enough. The climatology of the  $O_3$  distribution must be better established before reliable estimates of the surface sink can be made. Any future tropospheric measurement program should include surface and aircraft measurements of ozone to establish the magnitude of the Northern Hemisphere/Southern Hemisphere asymmetry.

Unlike stratospheric intrusions, which are associated with low water vapor concentrations and are readily detected from aircraft, *in situ* photochemical processes are widespread and quite difficult to observe directly. The design of any experiment to examine these processes must include the measurement of several important parameters in addition to ozone so that the chemistry and meteorology that accounts for the observed ozone distribution can be properly assessed. For example, Lenschow et al. (1981), employing fast-response  $O_3$  and meteorological sensors aboard an airplane, measured the flux divergence directly through a specified layer of the troposphere. Such an experiment yields the net *in situ* production (or destruction) within the domain, and thus the chemistry within this volume could be fairly well understood if concurrent measurements of  $NO_x$ ,  $CH_4$ ,  $CO$ , nonmethane hydrocarbons,  $H_2O$ ,  $CH_4O$ , UV flux, etc., could be obtained. Obviously, the uncertainty in the atmospheric chemistry would be reduced as the number and accuracy of the concurrently measured species increases. Such experiments must be made at several representative tropospheric locations and at as many different times of the year (to reflect varying meteorological regimes) as is feasible.

## TROPOSPHERIC CARBON CYCLE

The most abundant reactive carbon trace gases in the troposphere are methane ( $CH_4$ ) and carbon monoxide ( $CO$ ). Eventually, both of these species are oxidized to carbon dioxide ( $CO_2$ ), which is the primary carbonaceous trace gas in the atmosphere but is fairly unreactive in the troposphere. This section will be concerned primarily with reactive tropospheric carbonaceous trace gases. The discussion which follows will concentrate on the individual cycles of  $CH_4$ ,  $CO$ , and NMHC in order to present a comprehensive picture of the overall reactive carbon cycle in the troposphere. Some major components of the tropospheric carbon cycle are shown in figure 2.

### Methane

#### Scientific Background and Issues

Methane is an important component of the biogeochemical cycle of carbon with potentially critical roles in both atmospheric chemical and radiative transfer processes (Seinfeld et al., 1981). Considerable modeling and field research has been

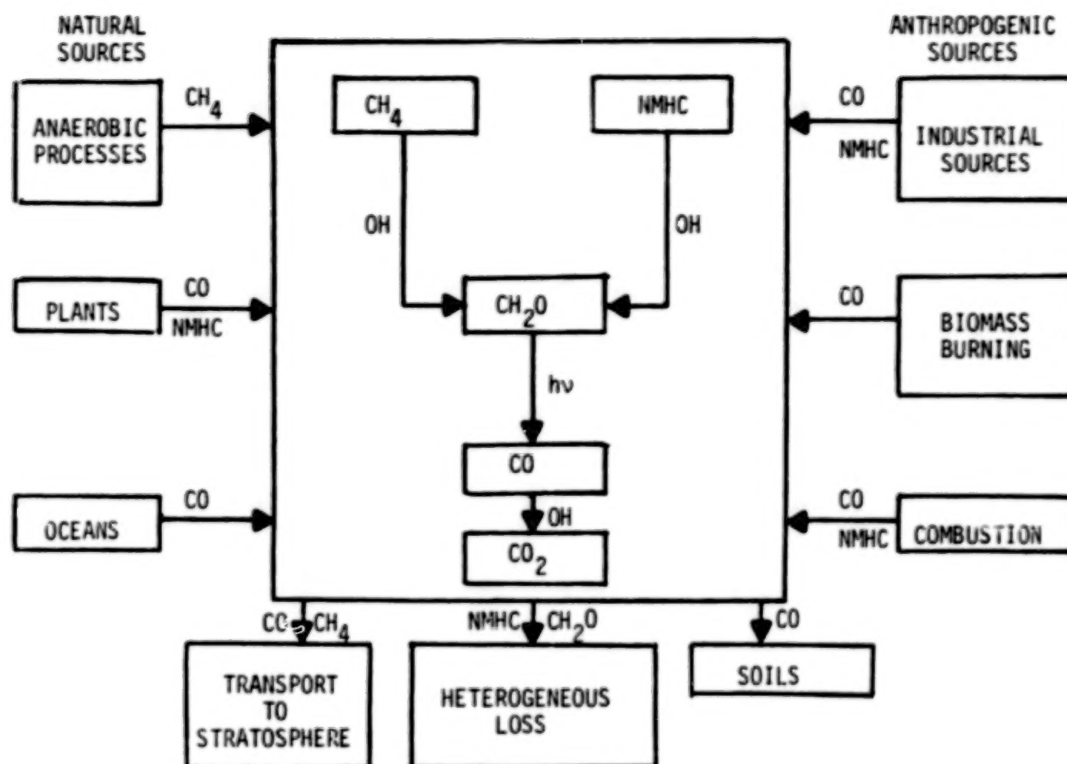


Figure 2. Tropospheric carbon cycle.

conducted which partially elucidates the key role of methane in global tropospheric air quality. Current understanding of the distribution, sources, and sinks of methane in the tropospheric boundary layer can be summarized as follows:

1. The tropospheric concentration of methane is approximately 1.65 ppmv (Heidt and Ehhalt, 1980); values greater than 2 ppmv have been commonly observed in urban atmospheres and in the vicinity of natural gas fields (Scranton et al., 1980; Dianov-Klokov et al., 1977).

2. A 0.1-ppmv interhemispheric gradient in methane concentration has been measured, with higher values in the Northern Hemisphere (Ehhalt, 1978). The concentration gradient may be due to the spatial distribution of sources and/or changes in the concentration of other atmospheric gases, such as  $\text{CO}$  and  $\text{OH}$ , which influence the photochemical destruction rate of methane.

3. Several lines of evidence suggest that tropospheric concentrations of methane are increasing. Graedel and McRae (1980) reported an increase in methane over the past decade at a suburban location in New Jersey. Rasmussen and Khalil (1981a) observed a 1.9 percent per year increase in atmospheric methane concentration during a 2-year (1979-1980) monitoring program at Cape Mears, Oregon

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(45°N). The latter data set also exhibits considerable seasonal variability which is unexplained at present. Fraser et al. (1981) have observed a 1.2 percent per year increase in atmospheric methane at Cape Grim, Tasmania (41°S).

4. Existing estimates of global sources of methane released to the troposphere are highly uncertain (table 1). Recent studies on wetland sources (rice paddies, swamps, river floodplains, etc.) demonstrate a 100-fold variation in emission rates of methane related to both natural and anthropogenic factors (table 2). It appears reasonable to expect that a more extensive program of flux measurements will provide the basis for a reasonably quantitative estimate of the role of wetlands as a global source of atmospheric methane. Other sources (e.g., combustion, animals, etc.) also require quantification.

TABLE 1. MAJOR SOURCES OF ATMOSPHERIC METHANE\*

Source	Annual production, $10^{12}$ g CH <sub>4</sub> yr <sup>-1</sup>
Biogenic	
Swamps, marshes	190 to 300
Wetland agriculture (rice)	280
Enteric fermentation (animals)	100 to 220
Enteric lakes	1 to 25
Tundra	0.3 to 2
Oceans	1.3 to 16.6
Anthropogenic	
Coal and lignite	7.9 to 27.7
Industrial	7 to 21

\*Data summarized from Ehhalt and Schmidt (1978). All of the annual production estimates listed in this table are based on extrapolation from a very limited data base.

### Proposed Field Measurements

The top priority measurements for gaining an improved understanding of the global methane cycle should be focused on quantification of terrestrial biogenic sources and the role of the oceans as a source and/or sink. Several types of sampling and measurement approaches will contribute critical data, such as:

TABLE 2. COMPARISON OF MEASURED METHANE FLUXES FROM  
FRESHWATER WETLANDS

Site	Flux, g CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> *	Ref. <sup>†</sup>
Michigan swamp	0.52	1
Michigan farm ponds	0.52	1
Rice paddy (open water)	0.004	2
Rice plants (unfertilized)	0.032	2
Rice plants (fertilized)	0.15	2
Virginia swamp	0.008	3
S. Carolina cypress swamp	0.01	3
Georgia cypress swamp	0.09	3
Florida cypress swamp (fertilized)	0.97	3
Florida cypress swamp (unfertilized)	0.067	3

\*All flux measurements used for this comparison were made in the soil temperature range 20° to 29°C.

†References:

1. Baker-Blocker et al. (1977)
2. Cicerone and Shetter (1981)
3. Harriss and Sebachner (1981)

1. An enhanced program of ground-based methane flux measurements, with careful corollary measurements of other biogeochemical variables (e.g., soil water content, organic content, temperature, etc.), should be conducted in potential source areas such as wet tropical forests, swamps, salt marshes, and tundra ecosystems. Selection of experimental sites should take into account ongoing ecological research, primarily sponsored by the National Science Foundation Ecosystem Studies Program, where data on nonmethane carbon fluxes and other environmental



variables will be available. Careful attention should be paid to both temporal and spatial variations in methane flux within any particular ecosystem.

2. Because many of the natural areas for potential emission of methane to the boundary layer are remote, presenting extreme difficulties to ground-based flux measurements, a low-altitude flux measurement program should be attempted. Meteorological measurement techniques, described by Lenschow et al. (1980, 1981), might be combined with the NASA gas-filter-correlation infrared methane detection system (Sebacher and Harriss, 1982) to determine large area methane flux in the boundary layer. A necessary first step in preparing for aircraft flux measurement capabilities for methane would be to test the response time, precision, and accuracy possible with the gas-filter-correlation system. Preliminary test flights for methane flux should be conducted over a natural gas field or other strong source.

3. Factors which influence the solubility of methane in sea water and the exchange rate of methane across the air-sea interface are poorly understood. The currently popular hypothesis that the ocean is neither a significant source nor sink in the global methane cycle is based on very limited data. A set of coordinated laboratory and field measurements is needed to examine the effects of dissolved organic materials, pH, microbubbles, and methane oxidizing bacteria on water column concentrations of methane. Quantification of the influence of surface films and ocean surface roughness on methane exchange rates across the air-sea interface is also an important research need. (See Broecker et al. (1980) for an assessment of similar problems related to  $\text{CO}_2$  exchange.)

Existing data indicate that the most significant marine methane sources are probably in coastal environments (Atkinson and Hall, 1976; Martens and Klump, 1980). Experiments are needed to determine the significance of habitat (e.g., tidal creek, marsh grass, etc.) in methane source strength. Long-term monitoring needs to detect changes in global tropospheric methane concentrations will be discussed in a separate section of this document.

## *Carbon Monoxide*

### Scientific Background and Issues

The atmospheric cycle of CO has been studied in considerable detail. (See Seiler (1974) and Logan et al. (1981) for reviews.) However, major uncertainties remain concerning the distribution, sources, and sinks of CO. For example, there are very little data on seasonal variations in the nonurban troposphere and from the remote Pacific regions. Carbon monoxide has an atmospheric residence time of a few months; consequently, it essentially resides in the hemisphere where it is produced. This is thought to account for the higher concentration in the Northern Hemisphere. The primary CO sources are believed to be  $\text{CH}_4$  oxidation, various combustion processes (including automobile emissions and tropical biomass burning), and the photochemical oxidation of both natural and anthropogenically produced hydrocarbons (table 3). Estimates of the amount of CO produced from  $\text{CH}_4$  oxidation and direct industrial emissions are not known better than by a factor of 2; considerably more uncertainty exists for the contribution due to naturally emitted hydrocarbons such as isoprene and various terpenes. One of the major obstacles in the determination of how much CO may come from the oxidation of naturally emitted

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TABLE 3. GLOBAL CO BUDGET,  $10^{12}$  g CO yr<sup>-1</sup>  
(from Logan et al., 1981)

Condition	Total	Northern Hemisphere	Southern Hemisphere
Sources			
Fossil fuel use	450 (400-1000)	425	25
Oxidation of anthropogenic hydrocarbons	80 (0-180)	85	5
Oxidation of natural hydrocarbons	560 (280-1200)	380	180
Emissions by plants	130 (50-200)	90	40
Wood used as fuel	51 (25-150)	33	17
Forest wildfires	25 (10-50)	22	3
Forest clearing	380 (200-800)	260	120
Savanna burning	200 (100-400)	100	100
Ocean	40 (20-80)	13	27
CH <sub>4</sub> oxidation	<u>810 (400-1000)</u>	<u>405</u>	<u>405</u>
Total	2740 (1500-4000)	1820	920
Sinks			
Soil uptake	250	210	40
Photochemistry	<u>3170 (1600-4000)</u>	<u>1890</u>	<u>1280</u>
Total	3420	2100	1320

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hydrocarbons is the lack of an understanding of the oxidation mechanism of these species. If  $\text{CH}_2\text{O}$  (or other aldehydes) is primarily produced as an intermediate species in this oxidation process, then it is believed that the CO yield will be fairly high. However, it is quite possible that organic acids, organic peroxides, ketones, alcohols, and other organic intermediate species may be formed which may directly oxidize to  $\text{CO}_2$ , or may be conducive to removal by heterogeneous processes such as rainout, washout, or aerosol formation. It is clear that a better understanding of this oxidation mechanism is necessary before this CO source can be properly assessed.

Although tropical biomass burning has been proposed as an important source of CO (Crutzen et al., 1979), a lack of knowledge of where, when, and how this burning takes place greatly hinders an accurate quantification of this source. Continuous monitoring of the CO in the tropics by satellite would help in the determination of the magnitude of this source.

Direct emission of CO by plants, production by lightning, and release by the oceans have been identified as CO sources, but the importance of these sources on a global scale is currently believed to be small.

Soil uptake and oxidation by OH have been identified as the major sinks of atmospheric CO (table 3); in addition, a small fraction (approximately  $100 \times 10^{12}$  g  $\text{CO yr}^{-1}$ ) of the tropospheric burden is transported to the stratosphere where additional oxidation by OH takes place (Seiler, 1974). Reaction with OH is by far the most important sink for CO and, in turn, reaction with CO is believed to be the dominant removal mechanism for OH in the troposphere. Thus it has been hypothesized that OH levels could be suppressed if CO is allowed to build up in the troposphere. The result of such a scenario would reduce the ability of the troposphere to scavenge many trace gases as efficiently as it does now with the present levels of CO and OH. This, in turn, would allow larger amounts of  $\text{CH}_4$ , various chlorocarbons, and other trace gases to enter the stratosphere, thereby perturbing stratospheric chemistry.

## Proposed Field Measurements

Field measurement programs for CO should focus on obtaining a better understanding of the seasonal and latitudinal boundary layer and free tropospheric distribution of CO, while at the same time conducting simultaneous measurements of other important trace gases such as  $\text{O}_3$ ,  $\text{NO}_x$ , and  $\text{CH}_2\text{O}$ . The concurrent measurement of those other species should greatly facilitate any understanding of the sources and sinks that influence the global budget of CO.

## Nonmethane Hydrocarbons

### Scientific Background and Issues

Perhaps the greatest deficiency in understanding the reactive carbon cycle in the troposphere concerns the photochemistry and chemistry and global emission rates of nonmethane hydrocarbon (NMHC) species. Very few studies have considered the photochemistry and chemistry of NMHC in the global troposphere. (For example, see Chameides and Cicerone (1978) and Brewer et al. (1982).) NMHC's include alkanes, such as ethane ( $\text{C}_2\text{H}_6$ ), propane ( $\text{C}_3\text{H}_8$ ), and butane ( $\text{C}_4\text{H}_{10}$ ); olefins, such as ethylene ( $\text{C}_2\text{H}_4$ ) and propylene ( $\text{C}_3\text{H}_6$ ); alkynes, such as acetylene ( $\text{C}_2\text{H}_2$ ); aldehydes, such as formaldehyde ( $\text{H}_2\text{CO}$ ) and acetaldehyde ( $\text{CH}_3\text{CHO}$ ); peroxyacetylnitrate



( $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ); isoprene; and terpenes. Alkanes, olefins, and alkenes are emitted from anthropogenic sources, while isoprene and terpenes are emitted from vegetation. The remaining species are chemically produced from the oxidation of the emitted species by OH,  $\text{O}_3$  and  $\text{O}(^3\text{P})$ . Oxidation of the simpler NMHC's (ethane, ethylene, and acetylene) produces the same products that are produced from the oxidation of  $\text{CH}_4$ , namely  $\text{H}_2\text{CO}$ , CO,  $\text{CH}_3\text{OOH}$ ,  $\text{CH}_3\text{O}_2$ , and  $\text{CH}_3\text{O}$ ; in addition, the peroxyacetyl radical ( $\text{CH}_3\text{C}(\text{O})\text{OO}\cdot$ ), the radical precursor to peroxyacetyl nitrate (PAN), is produced. The longer chain hydrocarbons are sources of longer chain radicals (such as the ethylperoxy ( $\text{CH}_3\text{CH}_2\text{O}_2$ ) and ethoxy ( $\text{CH}_3\text{CH}_2\text{O}$ ) radicals), which undergo reactions that parallel those in the  $\text{CH}_4$  oxidation chain. Interaction occurs only when reactions of longer chain NMHC's produce the same oxidation products that are produced in the oxidation of  $\text{CH}_4$ .

#### Proposed Field Measurements

Zimmerman et al. (1978) estimated that NMHC anthropogenic emissions account for about 10 percent of the total flux of NMHC's, while "natural" sources (of isoprene and terpenes) account for the remaining NMHC emissions. While the total NMHC anthropogenic emissions flux is fairly well characterized by emissions inventories, the breakdown of the total NMHC flux into fluxes for each bonding class is not well characterized. Further, measurements of anthropogenically emitted NMHC's have only been performed for the simplest species in each bonding class, i.e., ethane, ethylene and acetylene. (See, for example, Robinson (1978) and Rasmussen and Robinson (1977).) Measurements of profiles of acetaldehyde, formaldehyde, alkylperoxy and alkoxy radicals, and longer chain members of anthropogenically emitted NMHC's are needed to validate the NMHC chemical reaction scheme.

Less is known about the emission fluxes, chemical reactions, and species concentrations of isoprene and terpenes than about anthropogenic NMHC's. Since isoprene and terpenes are emitted by plants, the emission rates are determined by the vapor pressure of isoprene or the terpene species (which is directly dependent upon temperature); thus, emission rates of terpene species are more difficult to characterize than those of anthropogenic NMHC's. The chemical reactions of isoprene and terpenes are also not very well understood. Unlike the anthropogenic NMHC's, whose kinetics have been studied for urban-scale air pollution modeling, the terpenes have no direct impact on urban-scale air pollution. The short lifetimes of isoprene and terpenes due to chemical reactions further complicate chemical kinetic studies of their reaction rates. Zimmerman et al. (1978) postulated a mechanism for the reaction of OH with isoprene, but this mechanism has not been verified by laboratory studies. One method of inferring terpene emission rates is to measure profiles of the products of terpene and isoprene oxidation reactions. Such products should be measured in forested areas in several latitude bands, and measurements should certainly include the species formaldehyde and acetaldehyde. Concentrations of hydrocarbon intermediates such as alkoxy and alkylperoxy radicals measured in the same forested areas are also an important aid in verifying postulated terpene chemical mechanisms with models. Estimates of the percentages and types of forested areas within latitude bands are also required for model validation.

Another uncertainty in the chemistry of isoprene and terpenes is the product distributions obtained from terpene oxidation reactions. Product distributions have not been well characterized and are needed to conduct modeling studies which include terpene reactions. The lack of product distributions is due primarily to the experimental difficulties encountered in studying such reactions, in part

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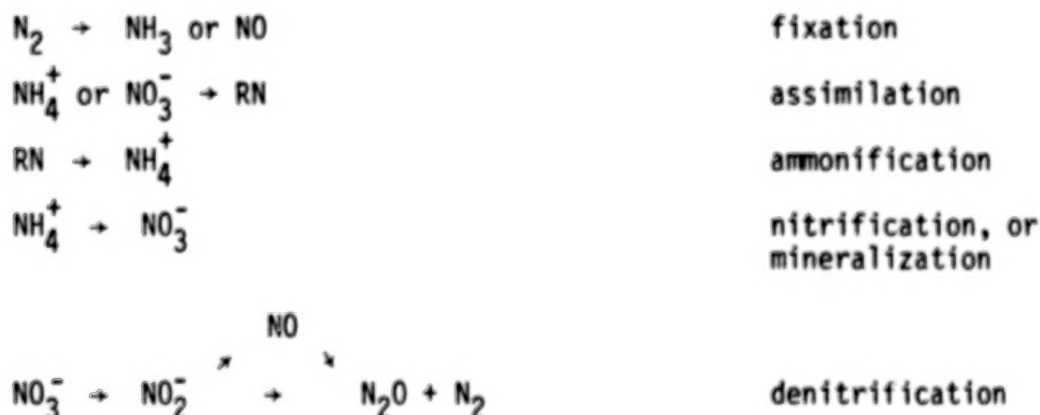
because of the short lifetimes of terpenes due to chemical destruction by oxidation. In addition, postulated products of terpene reactions are also short-lived; they react further to produce subsequent products. Rapid detection systems are required to characterize the products.

A comprehensive understanding of the distribution of C<sub>2</sub>-C<sub>8</sub> alkanes and olefins, with concurrent CO, O<sub>3</sub>, and NO<sub>x</sub> measurements, would help greatly to identify the role of these species in the global carbon and tropospheric ozone cycles. In addition, concurrent measurements of some intermediate species in the oxidation chain, such as formaldehyde, acetaldehyde, organic peroxides, peroxyacetylnitrate, ethylmethyl ketone, and others, would be beneficial. The gas-phase and heterogeneous chemistry of these intermediate species also needs to be better understood.

## TROPOSPHERIC NITROGEN CYCLE

### Scientific Background and Issues

The flow of nitrogen in various chemical forms through the air, hydrosphere, and soils constitutes a biogeochemical cycle. Rather than N<sub>2</sub> itself, which is, of course, the most abundant substance in the atmosphere, the most important nitrogen-containing species for life on Earth are the fixed or odd-N species. In these chemicals the individual N atoms are not bound to each other. In this fixed or odd form, nitrogen is useful and necessary in living organisms. The key processes in the global N cycle may be represented as follows:



In the N cycle the N<sub>2</sub> taken from the air is fixed either naturally or anthropogenically, and is eventually returned to the atmosphere as N<sub>2</sub>O and N<sub>2</sub>. A traditional view holds that NO may be, but is not necessarily, produced by denitrification, and N<sub>2</sub>O is produced solely by denitrification. Recent studies show that ammonia oxidation (nitrification) also yields some N<sub>2</sub>O (Lipschultz et al., 1981). A rich variety of phenomena (microbial, physical, and chemical) operate in these nitrogen cycle steps on land, air, and sea, and nitrogen exists in all eight possible oxidation states. (For reviews see Delwiche (1981) and National Research Council (1978a).)

Atmospheric nitrogen compounds exist in gaseous, liquid, and solid phase. Some are reactive, while others are relatively stable and long lived. Nitrogen is bound organically and in inorganic forms. As NH<sub>3</sub> (or NH<sub>4</sub>) and NO<sub>3</sub> it is a nutrient, but as NO, NO<sub>2</sub>, nitric acid, or organic nitrates and nitrites it is classified as a pollutant and is harmful to living creatures at high concentrations.

Key atmospheric reactions and processes internal to the nitrogen system include fixation (as NO) in lightning; formation of NO through the (stratospheric) reaction  $O(^1D) + N_2O \rightarrow 2NO$ ; oxidation of NO to NO<sub>2</sub> by O<sub>3</sub>, HO<sub>2</sub>, or organic peroxy species RO<sub>2</sub>; oxidation of NO<sub>2</sub> to HNO<sub>3</sub> by OH, or to NO<sub>3</sub> by O<sub>3</sub>; solar photolysis of NO<sub>2</sub> to release O atoms and NO; the incorporation of gaseous HNO<sub>3</sub> into liquid droplets and the aqueous formation of nitric acid; and the removal of all these species by cloud droplets, liquid-coated aerosols, and continental and marine surfaces. Stratospheric reactions, as well as the downward flow of stratospheric odd nitrogen into the troposphere, are also of global importance. (For reviews see Crutzen (1981) and National Research Council (1978a).)

The interactions of nitrogen species with other atmospheric chemicals (and with living systems) are also very important. In the troposphere and lower stratosphere, nitrogen oxides can result in the production of ozone through gas-phase reactions involving hydrocarbons, ozone, and sunlight. They also oxidize certain hydrocarbons and react rapidly with halogen oxides. Nitrates formed from nitrogen oxides strongly affect the chemistry of aerosols and hydrometeors; nitric acid is one of the two strong acids found in rainfall, and nitrosyl sulfuric acid is commonly found in atmospheric aerosol material. Ammonia as a proton acceptor is one of a very few basic compounds in the atmosphere. It can neutralize acidity, form complex ammonium nitrate and sulfate aerosols, and, when transported from one point to another, represents a transfer of fixed-nitrogen nutrient material.

For an approximate understanding of the global atmospheric nitrogen budget we must determine two of the following three quantities: (1) the annual source strengths, (2) the atmospheric (averaged) concentrations, and (3) the annual deposition (wet and dry) rate. For a more complete picture, we need all three of these quantities along with the identities of the individual species, the proportion of natural sources versus industrial sources, and spatially and temporally resolved source (emission) strengths and sinks (deposition rates). A further obvious point is that the mechanisms and rates of atmospheric transformations are also needed. More subtle questions must be answered if we are to predict future atmospheric nitrogen compound composition. We must determine which of the biological processes that produce fixed N or N<sub>2</sub>O are wholly natural and which are under human control. The extent to which human activities contribute to combustion processes, such as coal and wood burning, must also be established.

## *Proposed Field Measurements*

To characterize the atmosphere's nitrogen compounds and their budgets and allow several other important atmospheric processes to be understood properly (e.g., tropospheric ozone behavior and the chemistry of precipitation), a variety of measurements is needed. They may be grouped into source strength (emission rates and lightning fixation rates) measurements, deposition rate measurements, and atmospheric concentration measurements. In each of these categories, species-specific data are needed. In certain cases, total elemental fixed N data would be useful; all phases, gas, liquid, and solid, are involved. The needed spatial and temporal scales of the data are diverse. Of all the nitrogen-containing species mentioned above, only N<sub>2</sub>O is well characterized in the atmosphere as of late 1981. (E.g., see Weiss (1981).) Thus, while long-term measurement needs can be specified for N<sub>2</sub>O, the other N species are poorly measured in the troposphere, or are not measured at all. Therefore, many of the following requirements are for the short to intermediate term.



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The only odd-nitrogen source that is reasonably well known is the NO yield from high-temperature combustion. The fact that the U.S. EPA, DOE, and industrial entities are responsible for monitoring emissions of NO and NO<sub>2</sub> and the patterns and sources of these emissions suggests that further measurements are not required in NASA's program. Changing patterns of combustion and emissions control (both for stationary and nonstationary sources) must be recognized in NO source surveys, however.

Emissions of NO from nonindustrial pollution processes are much more difficult to estimate. These include small coal fires, wood burning, and biomass burning, the latter mostly in the tropics (Crutzen et al., 1979). Large-scale clearing of tropical forests is a regional process that recurs; large amounts of wood and vegetation are burned annually and these fires are amenable to sampling. As with all such processes, the conversion of measured concentrations into emission rates or fluxes of NO is risky.

The production of NO by lightning needs experimental verification and quantification. (E.g., see Levine et al. (1981).) The spatial variability, unpredictability, and hazard associated with lightning make *in situ* measurements difficult. Long-path optical measurements might be most feasible and could yield spatially averaged NO quantities. Lightning frequency and classification studies would permit extrapolation to annual zonal averages. Laboratory simulations are problematic due to difficulties in creating sparks of the correct detailed character and energies. Field studies of lightning yields should include measurements of NO<sub>2</sub> and possibly HNO<sub>3</sub>.

The likelihood that NO is released directly by soil microbial processes is high, but measuring release rates will be difficult, especially because of the spatial and temporal patchiness of available soil nitrate, amenable soil type, moisture, and other conditions. Exploratory measurements are needed, however. Similarly, the release of NO from NO<sub>2</sub> photolysis in ocean waters needs much more study. (E.g., see Zafiriou and True (1979).)

Ammonia releases from soils and from nitrogen-rich waste areas (e.g., animal feedlots and pastures) can be large regional sources (National Research Council, 1979). Other amines also need surveying. Similarly, NH<sub>3</sub>, HCN, and CH<sub>3</sub>CN can be products of biomass burning, especially if the fuel is nitrogen-rich and the fire smolders.

The spatial distribution and temporal trends now known for N<sub>2</sub>O can be explained with relatively small biogenic sources and a growing combustion source. The exact proportion of these sources is unknown and represents a question of growing importance. Much more survey work of individual combustion types (coal, oil, and natural gas flames) is needed. One might also suggest a search for <sup>15</sup>N, <sup>14</sup>N fractionation in atmospheric N<sub>2</sub>O, which might change with a changing mix of sources.

Sinks for atmospheric odd-nitrogen species are in need of as much attention as sources. An area particularly ripe for study is the simple monitoring of precipitation NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. Toward the goal of obtaining global deposition rates, we should begin to measure these quantities at a few fixed stations, including remote areas, polluted regions, and high fertilizer-usage areas. The National Atmospheric Deposition Program (NADP) and World Meteorological Organization precipitation chemistry network are steps in this direction. However, the deposition of NH<sub>4</sub><sup>+</sup>

and  $\text{NO}_3$  from aerosols must be measured simultaneously. The dry deposition of  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ , etc. is presently of unknown importance and the measurement of these rates is difficult. (See the review by Sehmel (1980).) As with the measurement of upward emission fluxes, the measurement of downward deposition fluxes will require attempts with different methods: meteorological, correlations, gradient methods, and possibly flat-plate collectors. Each of these methods must be deployed over varying terrain and conditions in sustained ways. Seasonal and zonal averages should be sought. (E.g., see Lindberg and Harriss (1981).)

Faced with an inadequate data base, one first seeks modest but much wider coverage for each species. While simultaneous measurements of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{O}_3$ , and  $\text{HNO}_3$  are needed, even isolated data are still useful. Methodical measurements of these species and  $\text{NH}_3$  in nonurban continental areas (with attention to the meteorologically variable fields), with vertical profiles, are needed for each season. Similar data from marine areas at various latitudes are also sought. If these measurements are performed at coastal or island stations or on shipboard, care must be taken to distinguish the surf zone from low aerosol regions.  $\text{NH}_4$  and  $\text{NO}_3$  concentrations in continental and marine aerosols, with particle size data, are also needed. After all of the previously listed quantities are surveyed and characterized, the next generation of measurement requirements can be generated with more confidence and focusing. Accompanying efforts should be made to detect  $\text{HNO}_4$  in the upper troposphere,  $\text{HCN}$  and other nitriles, peroxyacetylnitrate, and other organic N species.

Now that a temporal trend and spatial distribution have been well measured for  $\text{N}_2\text{O}$ , we can confidently recommend a long-term high-quality monitoring effort. This need not be at more than one or two stations in each hemisphere. Because of the stability of  $\text{N}_2\text{O}$ , one could use discrete flask sampling, automated stations, or shipboard sampling for making measurements.

To obtain the mixture of source, sink, and species concentration measurements suggested in the previous section, NASA and its investigators will need a variety of instruments and platforms. While a number of measurements are needed quickly with presently available methods, we should also realize that improvement in measurement techniques is a necessity. Species-specific methods are essential for unambiguous data. Aircraft-worthy instruments are needed for latitude surveys and vertical profiling. Fast time responses are needed if meteorological correlation techniques are to be used for upward emission flux or downward deposition flux measurements. For certain species (e.g.,  $\text{HNO}_3$ ,  $\text{HNO}_4$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HCN}$ ) new methods are needed. For previously unidentified species, i.e., for exploratory work, universal detector instruments (e.g., mass spectrometers or infrared absorption instruments) are desirable. Other special needs include field instruments for ground monitoring stations and for field source and sink studies. To survey soils and water bodies for  $\text{NO}$  and  $\text{NH}_3$  emissions, for example, will require some new but not necessarily expensive or high-technology instruments. To make 10-Hz measurements of, say, downward-flowing  $\text{HNO}_3$  or upward-flowing  $\text{NH}_3$  will require more elaborate developments, such as tunable lasers suitable for field operations.

One of the less pleasant realizations of the last several years is that meaningful measurements of  $\text{NO}$  in background air will require ultrasensitive devices. Concentrations as low as 5 ppt might be involved for  $\text{NO}$ , and 10 ppt for  $\text{NO}_2$ . Even for  $\text{HNO}_3$  it seems necessary to be prepared to measure 20 ppt in some places.

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While ideally one can hope for ground-based instruments or space-based satellite instruments capable of providing vertical profile data for the odd-nitrogen species, these are only hopes at present. It seems impossible to avoid the use of research aircraft, balloons, and/or blimps in the next 5 to 10 years. Considerations of payload capacity, as well as the growing need for simultaneous, coordinated measurements of the nitrogen species, aerosols, insolation, meteorological variables, and the closely dependent chemicals of the hydrogen, sulfur, and carbon families and ozone, lead one to believe that research aircraft are a necessity. High-speed turbulence and wind sensors for these aircraft are essential devices, and are already available (Lenschow et al., 1978).

## TRACE METALS

### *Scientific Background and Issues*

In the last several years, analyses of the chemical composition of aerosols collected at remote locations have indicated that several trace metals, such as Hg, As, Se, Cd, and Pb, are enriched up to several orders of magnitude in these aerosols relative to average concentrations in crustal or oceanic particulate material (Zoller et al., 1974; Duce et al., 1975; Rahn, 1976; Duce et al., 1976; Boutron, 1980; Maenhant et al., 1979). The metals having the largest enrichments are those which have relatively high volatilities and which can be termed atmophile (Lantzy and Mackenzie, 1979). Many of these same metals have been found to be toxic at relatively low concentrations.

Early attempts to construct global biogeochemical cycles for some of these metals resulted in the conclusion that although man's activities are a source of these metals, natural sources other than particulate crustal or oceanic material may be even more important. These include biogenic volatilization (e.g., methylation), direct volatilization from the crust, emissions from vegetation and forest fires, volcanic emissions, and gaseous emissions from the sea surface.

Very little data exist on the flux of trace metals to the atmosphere from these sources. The SEAREX (Sea-Air Exchange) program, funded by the National Science Foundation, is attempting to measure the sea-air exchange of trace metals at remote marine locations. This program is concentrating on wet and dry deposition at the sea surface and the flux of sea salt into the atmosphere.

A second research program with global implications involves studies of trace element sources and transport to the Arctic. (See Rahn, 1981a.) This program involves ground-based sampling over a large portion of the northern polar region, with emphasis on identifying sources of elevated trace metal levels observed in Arctic aerosols.

Sampling of tropospheric aerosols and gases for trace metal analysis at altitudes more than a few meters above ground level has been very limited. Occasional aircraft collections have been made in plumes from power plants, smelters, and volcanos (e.g., Germani et al., 1981; Lindberg, 1980; Project RAVE (Research on Atmospheric Volcanic Emissions) currently sponsored by NASA). While improved definition of trace element emissions from specific sources is badly needed, a program of large-scale sampling of the trace element content of the global troposphere should be given top priority. It is particularly important that the composition of aerosol and gas-phase trace elements be determined in the remote, free troposphere as a reference for air quality assessments. Present practice of using



an average crustal rock composition for defining levels of atmospheric "enrichment" is not adequate for assessing anthropogenic impacts on global tropospheric air quality.

Energy production is a primary source of many trace elements to the atmosphere (Bertine and Coldberg, 1971; Nriagu, 1979). Most forecasts for future energy consumption predict a significant increase in global coal consumption in response to declining availability of petroleum (Hafele, 1981). Coal contains 3 to 60,000 times higher concentrations of most trace elements than oil (table 4). Thus, an increase in coal combustion will increase emissions of many trace elements to the atmosphere. Knowledge of present tropospheric trace element levels will be critical to an assessment of impacts of increased coal use on global tropospheric air quality. In fact, the level of global chronic mercury and lead pollution may already be undergoing an increase (National Research Council, 1978b; Harriss and Hohenemser, 1978; Settle and Patterson, 1980).

TABLE 4. RATIO OF THE ESTIMATED ABUNDANCE OF TRACE ELEMENTS IN COAL AND OIL

Element	Coal/oil	Element	Coal/oil
As	75	I	8
B	60,000	Mn	600
Ba	667	Mo	170
Be	20,000	Ni	1
Br	40	Pb	800
Cd	3	Sb	75
Cl	27	Se	11
Co	50	Sr	1250
Cr	900	U	220
Cu	37	V	1
F	167	Zn	25
Hg	10		

## *Proposed Field Measurements*

Knowledge of the distribution of trace elements in the troposphere above 10 meters from the ground is so limited that measurements at any location will be a useful contribution. However, top priority should be given to the following problems:

1. Advances in techniques for sampling and analysis from aircraft platforms will be a first priority for studies of tropospheric trace metals. Problems of particular importance include minimizing contamination during sampling, reducing sampling times to a minimum, and developing techniques which can quantitatively collect both gas-phase and particulate trace metals in the boundary layer and free troposphere. Chemical studies of the tropospheric aerosol will be aided by close collaboration with the development of lidar techniques for real-time measurement of aerosol distribution. The lidar data can be used to guide sampling of specific aerosol layers in the atmosphere.



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2. More information on the exchange of trace elements between the boundary layer and the free troposphere is vitally needed. The question of long-distance transport of trace metals is central to assessing future impacts of anthropogenic activities on global tropospheric air quality. Most anthropogenic emissions are released into the Northern Hemisphere boundary layer. A combined emissions inventory, ground-based sampling, and aircraft sampling program is needed to evaluate what fraction of trace metal emissions to the boundary layer is transported to the free troposphere with subsequent large-scale dispersion. Areas of particular interest are the Eastern U.S., the North Atlantic, and Northern Europe. A program of aircraft measurements would complement the ongoing Arctic Air-Sampling Network (Rahn, 1981b).

3. Preliminary studies should be conducted to assess the possibility of conducting direct active or passive remote measurements of trace elements which occur primarily as gaseous species. Elements of particular interest for tropospheric air quality research are mercury, arsenic, and selenium. Development of fast-response remote sensing techniques will permit investigation of interhemispheric exchange and other aspects of long-distance transport of trace metals.

4. Emissions of trace metals from large-scale natural high-temperature processes such as forest fires, agricultural burning, and geothermal vents are very poorly known and require quantification for comparison with anthropogenic sources. Ground and aircraft sampling will be required in a manner similar to that of the RAVE Project.

## TROPOSPHERIC SULFUR CYCLE

### *Scientific Background and Issues*

The sulfur cycle in the atmosphere is complex and poorly understood, and there are large discrepancies among different estimates of sources and sinks. However, it is apparent that both anthropogenic and natural sources are important. The principal anthropogenic source is fossil fuel combustion, with most of the sulfur emitted in the form of  $\text{SO}_2$  (although a small fraction is emitted as  $\text{SO}_3$  and  $\text{SO}_4$ ). The natural sources of sulfur are largely unknown and unquantified. A survey of the sulfur species believed to be present in the atmosphere has been compiled by Graedel (1977). Many reduced sulfur compounds ( $\text{CS}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{COS}$ , etc.) have both industrial and natural sources.

Sulfur compounds in the atmosphere are not believed to have significant impact directly on other trace gas cycles, but they are important from environmental viewpoints. For example,  $\text{SO}_2$  and sulfate from primary and secondary sources may be detrimental to human health at levels found in the continental U.S. and western Europe,  $\text{COS}$  may be responsible in large part for atmospheric corrosion (Graedel et al., 1981),  $\text{SO}_2$  and sulfate may contribute significantly to acidification of precipitation and surface waters,  $\text{SO}_4$  may play a major role in visibility reduction in the atmosphere, and the transport of  $\text{COS}$  from the troposphere to the stratosphere may influence global surface temperatures (Turco et al., 1980).

### Distribution and Sources of Sulfur Species

In nonpolluted areas there are typically higher  $\text{SO}_2$  values in the upper troposphere than in the boundary layer, higher  $\text{CS}_2$  values in the boundary layer

than in the free troposphere, and negligible DMS ( $\text{CH}_3\text{SCH}_3$ ) and  $\text{H}_2\text{S}$  in the free troposphere. COS has the highest ambient values and shows very little vertical variation. (See e.g., Flyger et al. (1970), Georgii (1978), Nguyen et al. (1974), Maroulis and Bandy (1977), Maroulis et al. (1978), Bandy et al. (1981), Jaeschke et al. (1978), Torres et al. (1980), and Lawson and Winchester (1979) for data.)

$\text{SO}_2$ ,  $\text{H}_2\text{S}$ , DMS, and  $\text{CS}_2$  are also present in sea water. The concentrations of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in the upper layers of the ocean are believed to be low due to the rapid oxidation to sulfate. Measurements of DMS and  $\text{CS}_2$  in ocean waters range from  $5 \times 10^{-13}$  to  $1.5 \times 10^{-9} \text{ g mL}^{-1}$  (Nguyen et al., 1978; Lovelock, 1974). The values depend strongly on geographical location. There is very little information on the COS content of sea water.

Although there is a developing climatology for certain species, there are very little vertical profile data, and a thorough survey of sulfur species present in various atmospheric regions has not been attempted.

The sources of atmospheric sulfur are many and are largely unquantified. The best known source is the emission of  $\text{SO}_2$  directly into the atmosphere as the result of fossil fuel combustion. These ground-level or near-surface sources are highly concentrated in certain geographical areas (eastern U.S. and western Europe). These sources and their impact on air quality are being investigated by a large number of investigators.

The direct sources of reduced sulfur are highly uncertain. Sources include microbial activity in soils and marshes, volcanoes, organic decomposition, forest fires, industrial activity, agricultural burning, livestock feed lots, and air-sea interactions. It is not known in what quantity, in what geographical areas, in what chemical forms, or under what conditions these sources are operative (let alone their contribution to the global cycle). For example, it is not known whether  $\text{CS}_2$  and DMS are of oceanic origin or whether the oceans are a source or sink of COS.

Many of the sulfur compounds in the atmosphere arise by chemical conversion of other forms. For example, gas-phase homogeneous oxidation of  $\text{SO}_2$  to  $\text{SO}_4$  occurs at rates of 0.1 to 3 percent per hour. In turn,  $\text{SO}_2$  can be produced from  $\text{CS}_2$ ,  $\text{H}_2\text{S}$ , COS, and DMS, and COS can be produced from  $\text{CS}_2$ . It is important to quantify what fraction of  $\text{SO}_2$ , COS, and  $\text{SO}_4$  is due to direct emission and what fraction is due to secondary production. This ratio will likely be influenced by location (urban, rural, continental, marine, etc.) and by the region of interest (boundary layer, free troposphere, stratosphere).

#### Homogeneous Chemistry

Homogeneous gas-phase chemistry of sulfur compounds is shown schematically in figure 3. Values of the rate constants have been studied by Richardson (1975), Kurylo (1978), Wine et al. (1980), Cox and Sheppard (1980), and Penkett et al. (1979b). The sulfur chemistry is highly dependent on the OH radical distribution.

However, there are still major discrepancies in the rate of the  $\text{CS}_2 + \text{OH}$  reaction. If the larger values are correct, then OH oxidation is the major sink. If, however, OH attack is slow then the photolysis of  $\text{CS}_2$  is important and may lead to a significant production mechanism for COS (Wine et al., 1981). COS, in turn, may be a major source of  $\text{SO}_2$  in the upper troposphere since it is believed that

little of the  $\text{SO}_2$  of boundary layer origin is transported to the upper troposphere. If this is true, then the  $\text{SO}_2$  in the upper troposphere must be produced *in situ*. These compounds are also important to stratospheric chemistry. Model studies by Turco et al. (1980) have shown that COS transported into the stratosphere may be a significant source of atmospheric aerosol in the Junge layer.

As indicated in figure 3, the ultimate fate of  $\text{SO}_2$  is oxidation to sulfate. The chemical formation of  $\text{SO}_4$  is a highly complex and poorly understood phenomenon including gas-to-particle conversions and heterogeneous catalysis, and  $\text{SO}_4$  interacts strongly with other chemical cycles (e.g.,  $\text{NH}_3$ , trace metals, graphitic carbon, and wind-blown dust).

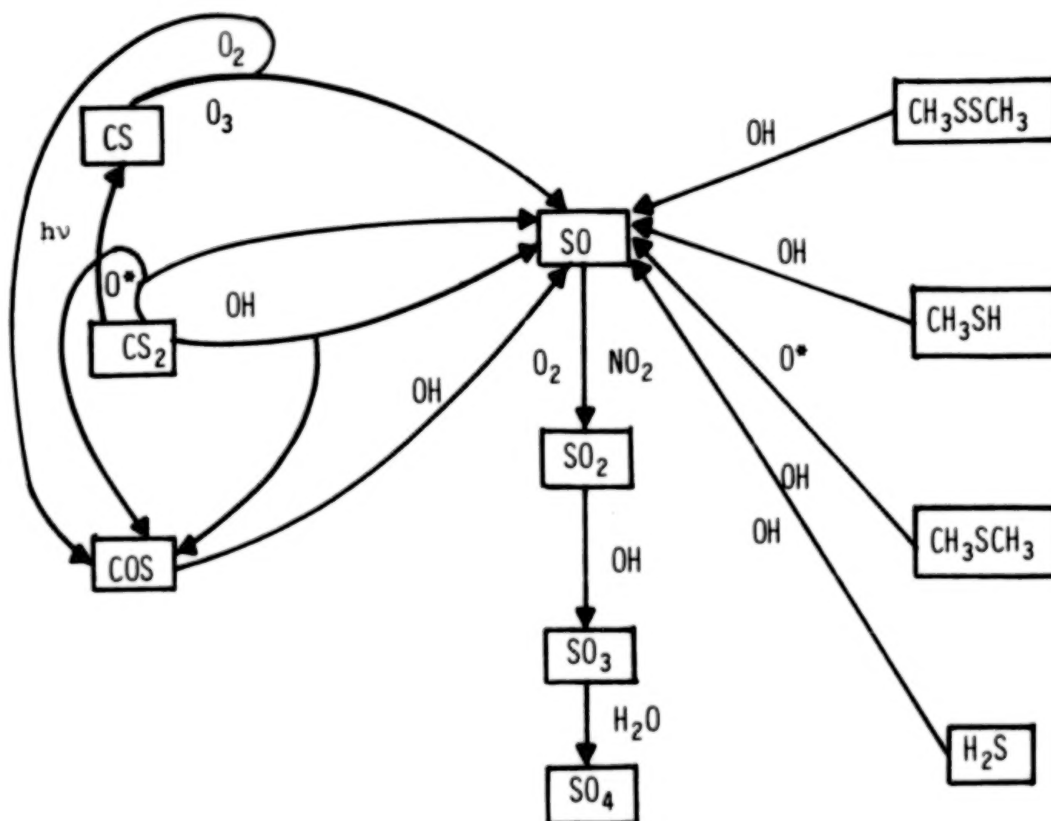


Figure 3. Sulfur cycle.

## Heterogeneous Removal

Heterogeneous removal processes are important in the atmospheric sulfur cycle. The removal of and reaction in dispersed liquid water droplets in the atmosphere (both in cloud and below cloud) represent both sinks (e.g., for  $\text{SO}_2$ ) and sources (e.g.,  $\text{SO}_4$ ) and greatly influence the vertical distribution and transport of sulfur compounds. For example,  $\text{SO}_2$  can be converted to  $\text{SO}_4$  at rates greater than 10 percent per hour in cloud droplets and rain water. Such processes are extremely complicated since it is also known that  $\text{NH}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , trace metals, and sulfur species all interact in solution chemistry. (For a review see Graedel and Weschler (1981).)

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Based on the current understanding of heterogeneous removal of reduced sulfur compounds it is hypothesized that in clouds boundary layer air loses its  $\text{SO}_2$  and particulate sulfate, whereas much of its  $\text{CS}_2$  and  $\text{COS}$  is transported to the free troposphere. This is believed to be true because the reduced sulfur compounds are only moderately soluble (solubilities similar to  $\text{CO}_2$ ). However, this hypothesis is highly speculative because of major uncertainties in the liquid-phase chemistry of these compounds.

## Dry Deposition

The removal (or destruction) of trace gases on surfaces can be an important sink process. In the case of  $\text{SO}_2$ , deposition on surfaces is as important as wet removal processes. The details of the mechanisms of surface removal are not well known; however, the process can be quantified experimentally. The experimental data are usually reported in terms of deposition velocity, with the data available on  $\text{SO}_2$  indicating deposition velocities of  $0.1$  to  $1.0 \text{ cm s}^{-1}$ . Current estimates for dry deposition velocities for sulfate fall in the same range.

Deposition velocity data are usually analyzed in terms of the aerodynamic and surface resistances. These resistances, in turn, depend on meteorological parameters (wind speed, atmospheric stability, temperature, cloud cover), surface roughness, type of vegetation or soil, time of year, and the surface evaporation rate. The current understanding of the deposition of  $\text{SO}_2$  and sulfate is such that meaningful estimates of dry deposition velocities can be made from measurements or estimates of the above variables. However, very little is known about the deposition rates of the reduced sulfur species and any estimate would be highly uncertain.

## Proposed Field Measurements

It is apparent from the discussions in the foregoing sections that there are many gaps in our understanding of the global sulfur cycle. The major questions that require answering in order to understand the cycle better are: (not in order of priority)

1. What reduced sulfur species are present in the atmosphere and what are their sources?
2. Is the ocean a source or sink of  $\text{COS}$ ?
3. What sulfur compounds are present in precipitation in different geographical regions and times of year?
4. What are the reaction rate constants for reduced sulfur-OH reactions?
5. What are the solubilities of reduced sulfur compounds?
6. What is the aqueous-phase chemistry of reduced sulfur compounds?
7. What is the hydrolysis rate of  $\text{COS}$ ?
8. How much  $\text{SO}_2$  emitted at ground level is transported to the upper troposphere? How much is produced *in situ* in the upper troposphere? What is the source of  $\text{SO}_2$  in remote areas?



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9. What is the principal sulfur-carrying species of oceanic origin?
10. What are the sources of  $\text{CS}_2$  and  $\text{COS}$  and what fraction is of anthropogenic origin?
11. What are the rates of surface destruction of reduced sulfur species?
12. What are the global distributions of  $\text{SO}_2$ , sulfate, and reduced sulfur species?

To answer these questions will require a combination of laboratory modeling and field studies. Clearly, questions 1, 2, 3, 8, 9, 10, 11, and 12 require field studies. Of particular importance are (1) survey studies to determine what sulfur species are present in different atmospheric regions, (2) vertical profile data over ocean upwellings, forests, continental areas in the Northern and Southern Hemisphere, etc., and (3) flux-type experiments to determine the rate of exchange of sulfur compounds between the boundary layer and the free troposphere.

The design of specific field studies should include single sampling sites within particular atmospheric regions where (1) a survey of sulfur compounds present in the air is obtained from GC (FPD) analysis, (2) a survey of sulfur compounds present in precipitation is obtained by similar analysis, (3) surface-based flux measurements are taken, (4) vertical profiles are taken, and (5) the frequency of measurements is such that diurnal and seasonal variations can be detected.

In addition, a field study designed to monitor the sulfur chemistry occurring in an air parcel as it travels from an urban region out over the oceans would provide valuable information on the sulfur cycle. This experiment would require that measurements of  $\text{SO}_4^-$ ,  $\text{SO}_2$ ,  $\text{COS}$ ,  $\text{CS}_2$ ,  $\text{H}_2\text{S}$ , and DMS be obtained simultaneously.

## MODELING RESEARCH TO SUPPORT SOURCE-SINK STUDIES AND BOUNDARY LAYER INFLUENCE ON THE FREE TROPOSPHERE

### *Multicycle and Multidimensional Models*

A comprehensive modeling effort must accompany a global research program. Within such a program, modeling studies will be required to understand many diverse phenomena. To accomplish this, small-scale microphysical processes should be well enough understood so that global-scale photochemical and transport models will provide a useful interpretation for the measurements which are obtained.

From a chemical point of view, it will be necessary to incorporate a comprehensive photochemical foundation which successfully describes the interdependence of the global carbon, hydrogen, oxygen, and nitrogen cycles. Most of the models to date have examined the carbon, hydrogen, oxygen, or nitrogen photochemical system using very simplified chemistry that excludes nonmethane hydrocarbons and transport. Such models can give some insight into the global-scale budgets of some trace gases, but generally they are inadequate to describe a particular set of measurements. As the tropospheric data base expands, multidimensional models will be required to explain the latitudinal distributions and seasonal variability inherent in these forthcoming data.

On the other hand, zero- and one-dimensional models must be developed to understand the very complex physical and chemical processes in the atmosphere. A good parameterization of these effects could eventually be incorporated into the more comprehensive global-scale models. Some specific complex chemical problems that affect the carbon-hydrogen-oxygen-nitrogen system include:

1. The chemistry of natural nonmethane hydrocarbons
2. Aqueous-phase chemistry, especially species which remove odd nitrogen and odd hydrogen from the atmosphere
3. The interaction of hydrocarbons and  $\text{NO}_x$  in polluted environments and how the exports from such regions impact the global tropospheric  $\text{O}_3$  and  $\text{NO}_x$  cycles

These examples are important, but they do not necessarily exclude other modeling studies that may be deemed relevant to future measurement strategies. An example of this concern is presented in the following section, which describes a continuing role for one-dimensional photochemical modeling.

## *Roles for One-Dimensional Photochemical Modeling*

During this period of planning and development of the next generation of tropospheric photochemical models (the so-called "multidimensional" models), the role of the one-dimensional photochemical model in future tropospheric research should be assessed. The multidimensional models, i.e., the two- and three-dimensional photochemical models, will combine atmospheric photochemical/chemical processes with a realistic representation of atmospheric transport. The incorporation of realistic atmospheric transport processes (as opposed to the prescribed vertical eddy flux coefficient representation in the one-dimensional model) will be an important advance in our understanding of the photochemistry/chemistry of the troposphere. Multidimensional models will enable, for the first time, the inclusion of localized natural and anthropogenic source locations for various species, and will permit studies dealing with the distribution of these species and their photochemical products as they are modified by various scales of atmospheric transport in the vertical and horizontal directions. However, it is evident that the increased storage requirements needed to include atmospheric transport processes in the multidimensional models will preclude the incorporation of such complete and detailed chemistry packages as are presently incorporated in the one-dimensional model. In addition, the inclusion of transport processes will greatly increase the running time and, hence, the cost of a calculation. It should also be noted that, to a first-order approximation, almost all tropospheric photochemistry/chemistry is initiated and controlled by the vertical transfer of solar radiation into and through the troposphere, as opposed to being initiated and controlled by horizontal transport processes. Clearly, the description of the vertical transfer of incoming solar radiation into and through the troposphere and its effect on the photochemistry/chemistry are most easily studied with the one-dimensional model. For the reasons briefly outlined here, it is believed that the one-dimensional photochemical model will continue to be an important tool in the hierarchy of the higher-order multidimensional models that are currently being planned and developed. The one-dimensional photochemical model is envisioned as the economical "workhorse" of tropospheric research over the next several years. The one-dimensional tropospheric model is particularly well suited to study the sensitivity of calculated species profiles to the uncertainties or deficiencies in our



understanding of various tropospheric physical and chemical processes. Some specific tropospheric problems that are particularly amenable to investigation with one-dimensional models are summarized below.

1. Studies are needed to assess the sensitivity of calculated profiles of various species to prescribed lower and upper boundary conditions. The global tropospheric budgets of  $O_3$  and  $NO_x$  may be strongly influenced by the flux of these species across the tropopause, yet there are large uncertainties in our understanding of the fluxes of these species across the tropopause and the effects of these fluxes on the vertical distribution of  $O_3$  and  $NO_x$  in the troposphere. One-dimensional model calculations have been used to assess the effect of various lower and upper boundary flux values for  $O_3$  and  $NO_x$  on the vertical distribution of  $O_3$  in the troposphere (Chameides and Stedman, 1977; Fishman and Crutzen, 1977; Liu, 1977; Liu et al., 1980).

2. Studies are needed to assess the effects of various possible chemical reaction pathways and/or poorly measured or ill-defined branching ratios and reaction rates on calculated species profiles. The oxidation chains of  $CO$ ,  $CH_4$ , non-methane hydrocarbons, and  $NH_3$  contain several possible reaction paths and poorly known branching ratios and reaction rates. The one-dimensional model can be easily and economically used to assess the sensitivity of the calculated species to various combinations of the ill-defined reaction scheme. For example, Brewer et al. (1982) used a one-dimensional photochemical model to investigate the effect of various possible reaction pathways and branching ratios on the vertical profiles of various nonmethane hydrocarbon species.

3. Studies are needed to assess the effects of various heterogeneous and physical loss processes on calculated species. The effect of various rainout rates on the vertical distribution of water soluble species, e.g.,  $HNO_3$ ,  $NH_3$ ,  $H_2SO_4$ ,  $H_2O_2$ , and  $HCl$ , can be assessed with a one-dimensional model. One-dimensional models can be used to study the photochemical formation of aerosols from gaseous species, e.g.,  $HNO_3$ ,  $NH_3$ , and  $H_2SO_4$ . Not only are we interested in understanding the chemistry of aerosol formation, which itself is an important problem, but the photochemical production of aerosols may also prove to be an important loss mechanism for  $HNO_3$ ,  $NH_3$ , and  $H_2SO_4$ . Some tropospheric species, e.g.,  $O_3$  and  $SO_2$ , are lost at the surface via dry deposition. The value of the deposition velocity which controls the depositional loss of these species is not well known. The one-dimensional model can be used to assess the effect of various values of the depositional velocity on the calculated species profiles.

4. Studies are needed to assess the effects of changes in the transmission of incoming solar radiation into and through the troposphere on calculated photolysis rates and species profiles. Changes in atmospheric transmission result from changes in the atmospheric aerosol burden and the presence of haze and various cloud types. For example, Augustsson and Levine (1982) have coupled a detailed model of the transfer of solar radiation into and through the troposphere to a one-dimensional photochemical model of the troposphere to assess the role of aerosol scattering and ground albedo on the vertical profiles of both photolysis rates and species.

5. Comparison of fixed-location ground-based or aircraft measurements of species profiles with calculated species profiles is needed to better understand the chemical and physical processes that control the species profile. For example, Levine et al. (1980) analyzed measurements of the vertical distribution of  $NH_3$

obtained with the Infrared Heterodyne Radiometer (Hoell et al. 1980) with a one-dimensional photochemical model. By varying various ill-defined model parameters, such as the loss of  $\text{NH}_3$  due to rainout, Levine et al. (1980) were able to deduce the value for rain-out loss that gave the best fit to the profile measurements. Using a one-dimensional model, profile measurements of species that result from surface emissions, such as  $\text{NH}_3$ , can be used to deduce emission fluxes.

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## STRATOSPHERIC-TROPOSPHERIC EXCHANGE

### INTRODUCTION

The various regions into which the atmosphere is classically divided are strongly coupled by several transport processes having a range of spatial and temporal scales. Some of these processes occur in complex physical structures such as tropopause folds or towering cumulus clouds. In addition, the mixing of air masses with differing chemical and physical properties may cause chemical and physical phenomena to occur which do not occur in other regions of the atmosphere. Studies of the interactions between differing regions of the atmosphere require specialized efforts because of these complications.

Studies of the exchange between the stratosphere and troposphere are needed in order to understand the global cycles of several materials such as  $O_3$  and  $NO_x$ . Some other species of interest are listed in table 5. It is important to understand the fluxes of these species as well as some of the chemical and physical processes which affect the chemicals during their transport.

At present a considerable body of experimental evidence exists on the process of transport from the stratosphere to the troposphere (Danielsen, 1968; Reiter and Mahlman, 1965); however, the fluxes across the tropopause of constituents such as odd nitrogen and CO have not yet been determined. Such measurements are required for a complete understanding of the global cycles of these materials. Although the flux of  $O_3$  has been determined perhaps to within a factor of 2 for the Northern Hemisphere, further work is also required. Modeling studies using general circulation models (Mahlman et al., 1980) show that the flux of ozone into the troposphere in the Southern Hemisphere is smaller than in the Northern Hemisphere. These flux differences could play a role in hemispheric differences in  $O_3$  levels. Experimental studies are needed to confirm this smaller flux. In addition, for many problems it is necessary to know the  $O_3$  flux into the troposphere to higher accuracy than a factor of 2. Evaluation of anthropogenic changes in  $O_3$  levels may also require higher accuracy. In addition, evaluation of tropospheric  $O_3$  sources is difficult, and to obtain a useful overall budget the stratospheric influx needs to be known accurately.

Although determination of the fluxes of various materials across the tropopause would be a major goal of a experimental program, it is also important to consider the possibility that unique chemical and physical processes may occur during the transport processes. For example,  $O_3$ -rich stratospheric air mixing with  $H_2O$ - and CO-rich tropospheric air represents a potential source region for substantial production of OH. This mixing process needs to be investigated to determine whether it is of significance for the global cycles of any chemicals. Also, chemical conversions of various kinds may occur in cumulus clouds penetrating the tropopause.

### *Chemicals Significantly Affected by Stratospheric-Tropospheric Exchange*

The interactions between the stratosphere and the troposphere must be considered in order to understand the global cycles of several chemicals of importance in the troposphere. In table 5 these chemicals are divided into two categories of exchange between the stratosphere and the troposphere. The first contains examples of species which are produced in the stratosphere and then transported into the

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TABLE 5. SPECIES OF INTEREST IN STRATOSPHERIC-TROPOSPHERIC EXCHANGE<sup>a</sup>

(a) Examples of chemicals produced in stratosphere and transported to troposphere

Species	Significance of source <sup>b</sup>
O <sub>3</sub>	Y
Odd nitrogen	D
Aerosols (sulfates)	D
Cl	N
H <sub>2</sub> O <sub>2</sub>	N

(b) Examples of chemicals active in the troposphere with stratospheric sink

Species	Significance of sink to tropo-spheric chemistry <sup>b</sup>
N <sub>2</sub> O	Y
CH <sub>4</sub>	Y
CO	D
SO <sub>2</sub>	D
NMHC	D
COS	N
Fluorocarbons	N
Condensation nuclei	N
H <sub>2</sub> O <sub>2</sub>	N
H <sub>2</sub> O	N

<sup>a</sup>Information useful for diagnostic studies of exchange includes radioactive tracers and potential vorticity.

<sup>b</sup>Y = high, D = possible, N = negligible.



troposphere. A designation of Y indicates that the tropospheric concentration is significantly affected by the stratospheric source, a designation of D indicates a possible effect, and a designation of N indicates only a negligible effect. The second category contains examples of species which are important for tropospheric chemistry and which are transported from the troposphere into the stratosphere, where they may have significant effects on stratospheric chemistry. A designation of Y, D, or N is used depending upon the significance of the stratosphere as a sink for the material and the significance of the material itself to tropospheric chemistry. For example, the stratosphere is a very significant sink for fluorocarbons, but they do not impact tropospheric chemistry strongly. Like-wise, COS is formed chemically in the troposphere but does not react further until it is removed in the stratosphere; hence fluorocarbons and COS are rated N. The first footnote includes examples of measurements which would be of great value in diagnostic studies aimed at understanding the physical processes which occur during exchange between the stratosphere and troposphere.

The presence of ozone is very important for tropospheric photochemistry. Levy (1971, 1973) has shown that ozone is a prerequisite in the production of hydroperoxyl and hydroxyl radicals, which control the chemical cycles of many important trace gases (e.g., CO, CH<sub>4</sub>, H<sub>2</sub>S, CH<sub>3</sub>, Cl, etc.) in the troposphere (Weinstock and Niki, 1972; Wofsy et al., 1972). Perturbation of ozone in the troposphere will change not only the chemical lifetimes of these species but also the radiation budget, and thus may affect the climate (Fishman et al., 1979a; Ramanathan and Dickinson, 1979).

The transport of ozone from the stratosphere has long been thought to be the dominant source of tropospheric ozone (Junge and Czeplak, 1968; Pruchniewicz, 1973; Fabian and Pruchniewicz, 1977; Chatfield and Harrison, 1976, 1977; Singh et al., 1978; Hussain et al., 1979). Estimates of this cross-tropopause ozone flux give values of about  $5 \times 10^{10}$  molecules cm<sup>-2</sup> s<sup>-1</sup> (Reiter, 1971; Cunlold et al., 1975; Danielsen and Mohnen, 1977; Mahlman et al., 1980). However, this concept of the origin of tropospheric ozone has been challenged by other investigators. Crutzen (1974), Chameides and Walker (1973), Fishman and Crutzen (1977), Liu (1977), Stewart et al. (1977a), Chameides (1978), and Fishman et al. (1979b) argue that the near-surface NO<sub>x</sub>, which is believed to be produced mainly by anthropogenic emissions, may catalytically produce more ozone in the lower troposphere than the cross-tropopause ozone flux. Recently Liu et al. (1980) proposed that the upper troposphere, where the stratospheric NO<sub>x</sub> mixes with tropospheric CO and H<sub>2</sub>O, is probably the dominant source region for ozone in the natural troposphere. Thus it is imperative that we understand the interactions between the stratosphere and the troposphere in order to understand the budget of tropospheric ozone.

The reason for including O<sub>3</sub> and odd nitrogen in table 5(a) is obvious from previous discussions. Cl<sub>x</sub> is transported into the troposphere in the same way as O<sub>3</sub> and odd nitrogen, but the flux is small compared to the chlorine in the sea-spray aerosols and is probably not important in the photochemistry of the upper troposphere. The transport of H<sub>2</sub>O<sub>2</sub> from stratosphere to troposphere or vice versa is also not important because its chemical lifetime is less than a day.

Table 5(b) lists a number of species with a significant chemical or radiative role in the troposphere which have tropospheric sources but have part or all of their sink in the stratosphere. N<sub>2</sub>O is mainly of interest in the troposphere because of its radiative properties. Absorption in the infrared can contribute to the greenhouse effect and thus affect the global surface temperature. (See, e.g.,

Yung et al., 1976; Wang et al., 1976.) The source of  $N_2O$  is in the biological cycling of fixed nitrogen in either the nitrification or denitrification step. (See, e.g., McElroy et al., 1976; Liu et al., 1977; Cicerone et al., 1978; Crutzen, 1972). Because of the increase in nitrogen fixation due to production of fertilizers, the possibility exists for increasing atmospheric  $N_2O$ . A small increase of approximately 6 ppb out of 300 ppb between 1970 and 1980 has been observed (Weiss, 1981), which implies a change in surface temperature  $\Delta T_s$  of approximately 0.012 K (Hansen et al., 1981). The only known significant sink appears to be the stratosphere, which therefore controls the tropospheric concentration and results in a lifetime for  $N_2O$  of 100 years or more.

Methane is another radiatively active gas that can contribute to the determination of surface temperature. Hansen et al. (1981) calculate a 0.033 K increase in temperature for an increase of 250 ppbv (out of approximately 1.6 ppmv). Others (Cicerone at this meeting; Rasmussen and Khalil, 1981a) claim that any observed changes are less than 100 ppbv. Methane is also of interest chemically because of its oxidation products, in particular CO. Other products of interest include formaldehyde ( $H_2CO$ ), hydrogen oxides (mainly  $HO_2$ ), hydrogen ( $H_2$ ), and possibly methyl hydrogen peroxide ( $CH_3OOH$ ). Methane loss occurs mainly via reaction with OH radicals in both the troposphere and stratosphere. The stratospheric loss is a few tens of percent of the total and is directly dependent on the adopted transport coefficients in the stratosphere.

Carbon monoxide is produced anthropogenically in combustion processes but other major sources include methane oxidation, oxidation of nonmethane hydrocarbons (NMHC), and biomass burning (Logan et al., 1981). CO is of very great interest chemically for two basic reasons: (1) it is the principal constituent limiting the OH concentration, via the chemical reaction which converts OH to H, and (2) it participates with the nitrogen oxides in a series of reactions which form ozone. CO is produced in both the troposphere and stratosphere (from  $CH_4$ ) and is destroyed in both (by reaction with OH). Since CO concentrations are significantly greater in the troposphere than in the stratosphere (as opposed to  $NO_x$  and  $O_3$ , which are greater in the stratosphere), it is of interest to consider the ozone production possible during a tropopause folding event, when  $NO_x$ -rich stratospheric air is mixed with tropospheric air rich in CO and other hydrocarbon oxidation products.

Nonmethane hydrocarbons (NMHC) include ethane ( $C_2H_6$ ), ethylene ( $C_2H_4$ ), acetylene ( $C_2H_2$ ), and isoprenes and terpenes. (See the section on nonmethane hydrocarbons.) They are sources for the same oxidation products as  $CH_4$ , i.e.,  $H_2CO$ , CO,  $CH_3OOH$ , etc., as well as a number of other more complex products such as peroxyacetylnitrate (PAN or  $CH_3C(O)O_2NO_2$ ). In general these species have their sources at the ground, either in combination or in biological processes, and their sinks via reaction with OH in both the troposphere and stratosphere. The importance of NMHC's as potential ozone producers is uncertain because their emission rates are very poorly quantified and their atmospheric chemistry is not well understood. Oxidation of some hydrocarbons may provide sources of or sinks for ozone.

The chlorocarbons include mainly fluorocarbon 11 ( $CFC1_3$ ), fluorocarbon 12 ( $CF_2Cl_2$ ), methyl chloroform ( $CH_3CCl_3$ ), carbon tetrachloride ( $CCl_4$ ), and methyl chloride ( $CH_3Cl$ ). Except for  $CH_3Cl$  and possibly  $CH_3CCl_3$ , these are anthropogenically produced. FC 11, FC 12, and  $CCl_4$  are all radiatively active and have their sinks almost entirely in the stratosphere.  $CH_3Cl$  and  $CH_3CCl_3$  both react with OH and can thus be destroyed in both the stratosphere and troposphere.  $CH_3CCl_3$  is of



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particular interest because it is reasonably well characterized, its concentration has been measured since 1972, and it is removed from the atmosphere by reaction with OH in the troposphere. Consequently, analysis of the budget for  $\text{CH}_3\text{CCl}_3$  provides a useful test of models for tropospheric OH.

The species listed in table 5 are candidates for field measurements designed to improve our knowledge of the fluxes between the troposphere and stratosphere. The highest priority species for studies of tropospheric global chemical cycles are those chemicals with large stratospheric sources, such as  $\text{O}_3$  and odd nitrogen. The next highest priority for study are species of significance to tropospheric chemistry or radiation with important stratospheric sinks, such as  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CO}$ .

## Transport

The Earth's troposphere is a complex chemical system influenced by *in situ* chemistry and tied together by transport. Although transport affects all chemical species, those with half lives on the order of  $10^5$  to  $10^8$  sec will survive long enough to become correlated with quasi-conservative meteorological variables. These correlations can be used both to study and confirm transport processes and, conversely, to establish a rationale for quantitative extrapolations of limited *in situ* chemical measurements to a global scale. For example, quantitative estimates of the transport into the troposphere of trace species generated in the stratosphere, such as ozone and odd nitrogen, can be based on correlations between *in situ* measurements and the potential vorticity.

Potential vorticity, a quasi-conservative meteorological tracer, is generated in the stratosphere by gradients of diabatic heating (radiative heating increasing with height) and is destroyed near the Earth's surface (heating decreasing with height). (See Appendix C for a discussion of potential temperature and potential vorticity.) Excluding the effects of diabatic heating due to the phase changes of water (condensation heating and evaporative cooling with clouds), the potential vorticity of a small air parcel is approximately conserved as it is transported through the atmosphere. However, the local mean value of a bulk air parcel is not conserved due to the effects of smaller scale mixing. Mixing does not destroy a correlation between the potential vorticity and the mixing ratio of trace species if and when they are correlated on a larger scale.

We know from *in situ* measurements and numerical general circulation experiments that ozone, radioactivity, and potential vorticity are positively correlated in the lower stratosphere as a result of mixing, despite the disparity in their latitudinal sources. We also know from aircraft and balloon experiments that when this lower stratospheric air enters the troposphere by tropopause folding, mixing reduces the magnitude of each quantity in a comparable way. Therefore, where large values of ozone are measured in the troposphere, a positive correlation with radioactivity (of stratospheric origin) and potential vorticity assures a stratospheric source for the ozone. Conversely, a negative correlation (an inverse functional relationship) implies a tropospheric source. Simultaneous measurements of other chemical species with a known surface or lower tropospheric source provides a rationale for confirming the implication. For example, when water vapor, carbon monoxide, and radon daughters are positively correlated with the ozone and negatively correlated with potential vorticity, this confirms the low-level source.

These correlations themselves emphasize an important distinction - the difference between tropospheric air and air which is temporarily at what are normally considered tropospheric levels but which is destined to return to the stratosphere. Air with high potential vorticity is not dynamically stable in the troposphere (as a balloon would not be buoyantly stable under water). Either the excess potential vorticity is destroyed by diabatic or turbulent processes or the air will return to the stratosphere, perhaps during the passage of an associated cyclone. Without mixing processes, which are more likely along the borders of the air mass, air with high potential vorticity will not come in contact with tropospheric air containing gases of surface origin (as air inside a balloon will be kept separate from dissolved gases in the surrounding water). The ozone measured in air with high potential vorticity will not be directly participating in tropospheric chemistry. For this reason emphasis in any observational program must be on the magnitude of this mixing.

The rationale for extrapolating limited *in situ* measurements to larger scale (subglobal or global) is based on identifiable and quantifiable large-scale meteorological structures. Again, due to mixing processes, quasi-homogeneous regions separated by large gradient transition zones can be objectively analyzed from synoptic meteorological measurements. These measurements include those obtained from the standard radiosondes (at fixed locations and times), aircraft, and satellite platforms. The analysis methods must remove from these data the distorted and incomplete signals produced by short-wavelength internal gravity waves to determine representative and dynamically balanced fields of the large-scale potential temperature, winds, vertical velocities, and potential vorticity.

#### PROPOSED FIELD MEASUREMENTS

##### Measurement Programs

Two types of measurement programs are envisioned: (1) measurements of the fluxes between the stratosphere and troposphere, and (2) studies of the processes affecting the chemicals during transport.

Measurements of the fluxes require attention to both the eddy flux component and the mean flux component. The eddy fluxes represent transport by small-spatial-scale turbulent winds, which may be correlated with deviations of the concentrations of the species from the mean concentration. The mean flux represents transport over wide geographic regions by the average wind field. The eddy flux would be determined by high-sampling-rate measurements (approximately one sample per second at typical jet flight speeds) of the species concentrations together with the vertical velocities (Lenschow et al., 1981). Such measurements also need to be made over horizontal distances on the order of 1000 km in order to determine the larger variations.

After removing large spatial-scale gradients from the concentration measurements, the eddy flux can be computed directly from these high-frequency wind and concentration measurements. The mean concentration and its gradients over the large spatial scale would then be used to find the mean flux. Models must be used in order to calculate the mean vertical velocities (which are too small to measure directly) from the large-scale meteorology.

In order to study the physical and chemical processes which occur during transport, many more kinds of measurements are required than are needed to compute

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fluxes. First, it is necessary to measure not only the chemical of interest but also other chemicals with which it might react, as well as various tracers. Of particular value are correlative measurements of the chemical and an inert tracer conserved in the absence of mixing or chemical reactions. Hence the correlation of measurements provides evidence for mixing rates, diabatic processes, and chemical conversion.

### *Regions of the Atmosphere in Which Measurements Would Be Conducted*

The two types of studies mentioned previously need to be conducted in several different regions of the atmosphere. Materials are believed to enter the stratosphere in the tropics primarily as the result of penetrating cumulus cloud towers. Studies of this process are very complex and would require at least two aircraft. High-altitude aircraft would be used to measure species concentrations at the cloud top, while lower altitude aircraft would be used to determine species concentrations at the cloud base and in the air surrounding the cloud. The scientific return from this type of experiment would be an improved understanding of the importance of cumulus cloud towers in tropospheric-stratospheric exchange.

A second experiment would involve studies of the injection of materials into the stratosphere in midlatitude tropopause folds. Such experiments would use a high-altitude aircraft. These studies are currently planned by the NASA Upper Atmosphere Research Program and would also be of great interest for tropospheric chemical studies.

The third experiment would consider the injection of ozone- and  $\text{NO}_x$ -rich stratospheric air into the troposphere at midlatitude tropopause folds. Such events would lead to mixing of  $\text{O}_3$ - and  $\text{H}_2\text{O}$ -rich air, with subsequent chemistry that would differ from that found in much of the troposphere and stratosphere. The chemistry most significantly affected from the point of view of global cycles would be that occurring over time scales of several days. Studies should be made in both the Northern and Southern Hemisphere. The Southern Hemisphere flux is expected to differ from that of the Northern Hemisphere because the dynamics differ (Mahlman et al., 1980). The scientific return from this type of experiment would be an improved understanding of the importance of tropopause folds in tropospheric-stratospheric exchange.

In the tropopause fold investigations, while the small-scale nature of the exchange must be observed, it will be most important to determine the temporally and spatially integrated effect. Of interest is the net effect of the exchange on the troposphere (and stratosphere) after air which has descended to tropospheric heights has had an opportunity to return to the stratosphere (as would be its tendency if it maintains high potential vorticity). This can be achieved by space- and time-averaging of concentrations below and above the tropopause before and after folding events.

After considering the potential scientific return from each of the experiments discussed previously and the relative difficulty and resources required for each, the workshop participants agreed that the tropopause fold experiments should be given first priority.



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## PROPOSED MODELING RESEARCH

Modeling activity needed to support these field experiments includes both regional or local models focused on analysis of the chemical and physical processes associated with exchange of ozone and other constituents between the stratosphere and troposphere, and large-scale models which help define measurement and sampling strategy and place the field measurements in global context. Simple models should be used to evaluate the importance of large quantities of  $O_3$  and  $H_2O$  being present simultaneously in the atmosphere. If the simple models reveal important chemical activity, then more realistic models should be constructed.

Simple models of the transport of gases into the stratosphere by cumulus towers might also be constructed. These models should investigate the importance of gaseous solubility in determining whether materials are carried into the stratosphere or removed by precipitation.

Global models will play an important role in defining as well as interpreting field measurements. This interplay is just beginning, but it will increase as our knowledge of the processes improves and our requirements for accuracy increase. At an early stage, the models and our current understanding of global dynamic processes can influence the measurements and sampling strategy for investigating stratospheric-tropospheric exchange. Important regions appear to be the mid-latitudes, where tropopause folding occurs, and low latitudes, where the Hadley circulation, driven by penetrating cumulus clouds, is probably the main source of exchange. It seems desirable to obtain observations during sudden stratospheric warmings, when exchange may be maximized, as well as under more normal circumstances. Global models can illuminate expected seasonal variations, and thus specify appropriate dates for observation, and can also contribute to establishing vertical, horizontal, and temporal sampling needs.

The need for global modeling is likely to increase in the future as detailed observational data begin to be analyzed and as the accuracy with which we can describe the atmospheric composition increases. A more detailed discussion of large-scale modeling is contained in the following section of this report on fast photochemical processes in the free troposphere.

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## FAST PHOTOCHEMICAL PROCESSES IN THE FREE TROPOSPHERE

### PROPOSED MODELING RESEARCH

Modeling is an essential element in a program designed to understand the chemical behavior of the troposphere. Utilization of mathematical models is required both for interpretation of the data obtained in field measurements programs and for aiding in the design of experiments to acquire data sets of optimum value. The report of the NASA Working Group on Tropospheric Program Planning (Seinfeld et al., 1981) emphasized the need for continued development of global scale tropospheric models and assessed their current areas of application. The modeling discussion presented herein will describe in more detail the relationship of individual model development activities to the projected fast photochemical field measurements program and to the ultimate objectives of the development of global prognostic models.

It should be borne in mind that in most cases the variables computed in model studies are not the same as those obtained in a single field measurements experiment. Most models treat species concentrations averaged over spatial and temporal domains differently from those in field measurements. It is not feasible to attempt to acquire the statistically significant data base required for validation of global models. Models are also characterized by large numbers of parameters (e.g., eddy diffusivities and chemical rate constants), the values of which are uncertain to varying degrees. Modeling is thus a process of inference, not of proof. Typically, numerous sensitivity studies are necessary to estimate the effect of parameter uncertainties on model results when there are only sparse observational data for comparison. This is an essentially qualitative procedure.

The interaction between modeling and field measurements is an iterative one. From an observational data base acquired from field measurements, constraints on model parameters are increased and the increasingly quantitative results help determine efficient sampling strategies.

Those modeling activities specifically related to fast photochemistry in the troposphere will include the following areas:

1. Development of fast photochemical models
2. Development of regional scale models
3. Development of models of combined homogeneous and heterogeneous processes
4. Development of diagnostic and prognostic models
5. Development of 3-D global models with parameterized chemistry

### *Fast Photochemical Models*

These models are designed to evaluate our understanding of the photochemistry of species having chemical lifetimes much smaller than their transport times. Since these models calculate species concentrations at a single temporal and spatial location (or a group of such locations), they are the only models which may be directly validated by a single field measurement experiment. Such validation is

necessary to the utilization of fast photochemical reaction schemes in models which treat coupled transport and photochemistry. There is, however, the unresolved problem of the possible effects of turbulent fluctuations on effective chemical reaction rates, as noted subsequently.

A fast photochemical model is described by:

$$C_i = P(C_j) / \ell(C_k) \quad (1)$$

where  $C_i$  is the concentration of a short-lived chemical species such as OH,  $P(C_j)$  is its chemical production rate,  $\ell(C_k)$  is its chemical loss coefficient, and  $C_j$  and  $C_k$  represent the concentration of species on which  $C_i$  depends. If  $C_i$  is the hydroxyl radical, then the set  $C_j$  and  $C_k$  would be comprised of at least  $O_3$ ,  $H_2O$ ,  $CH_4$ , and  $CO$ . Validation of equation (1) consists of measuring  $C_i$ ,  $C_j$ ,  $C_k$ , and meteorological variables on which chemical rate coefficients may depend with the same temporal resolution. In the case of the hydroxyl radical the chemical lifetime is about 1 second. Measurements of all the variables entering equation (1) with this temporal resolution would thus permit validation of the instantaneous photochemical model. On longer time scales it is possible that turbulent fluctuations of concentrations about their means will alter the effective chemical rate coefficients. If we assume that the instantaneous concentrations may be expressed as a mean and fluctuation about the mean, i.e.,

$$C_i = \bar{C}_i + C'_i \quad (2)$$

then substitution of equation (2) into the rate equations governing the  $C_i$  and averaging over an arbitrary time results in the appearance of second- and higher-order moments whose magnitudes are unknown. The effect of these correlations has been considered for idealized, two-component reacting systems (O'Brien, 1971; Donaldson and Hilst, 1972; Hilst, 1973; Hilst and Donaldson, 1973; Hilst et al., 1973). The problem of the effects of turbulent fluctuations on the set of chemical reactions in a relatively complex system, such as that governing OH in clean air, is unresolved. If the model

$$\bar{C}_i = P(\bar{C}_j) / \ell(\bar{C}_k) \quad (3)$$

could be shown to be essentially equivalent to equation (1), then the constraints on temporal resolution of measurements required to validate equations (1) or (3) could be relaxed. The task of describing photochemical effects in global models could also be carried on as it is currently, without regard to effects of turbulent fluctuations.

## Regional-Scale Models

The development of regional scale models is essential to an understanding of the interactions between tropospheric domains having different physical and biological characteristics. For example, if the region being studied is characterized by large emissions of industrial effluents, such models could estimate the effective global source strengths due to pollutant sources of relatively small extent. Gross emissions inventories are inadequate since the effluents will generally undergo transport and chemical transformation in environments atypical of other tropospheric regions into which they ultimately intrude. Parameterization of sub-grid-scale emissions in global models is an example of a problem which will be facilitated by regional-scale modeling. Regional modeling is not restricted to the



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interaction of industrial emissions with other tropospheric areas; depending on future developments it may be applied to any of the "representative" tropospheric domains described by Seinfeld et al. (1981).

Understanding fast photochemical transformations in various tropospheric regions is dependent on the sources and sinks of longer lived species characteristic of those regions. Field measurements must be designed with the specific characteristics of the target region in mind. It is desirable to concentrate initially on those regions presently believed to be least complex chemically. These will include remote regions far removed from anthropogenic sources.

### *Heterogeneous Processes*

Many trace species are removed from the atmosphere by precipitation, attachment to aerosols, or destruction at the Earth's surface. For example, the fast photochemical cycles involving  $\text{NO}_x$  and  $\text{HO}_x$  are terminated by rainout of the soluble gases  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$ , while aerosol chemistry is important for removal of  $\text{SO}_2$ ,  $\text{NH}_3$ , and possibly  $\text{H}_2\text{O}_2$ . Ozone, sulfur species, and  $\text{HNO}$  undergo loss at the Earth's surface. (See reviews by Garland (1978) and Galbally and Roy (1980).)

These processes are crudely parameterized in present models of the global troposphere. Rainout is treated as a first-order loss process with the loss coefficient dependent on altitude or rainfall rate, while the rate of deposition of a gas at the Earth's surface is calculated from an experimentally determined deposition velocity. In general, reactions involving aerosols are not considered unless sulfur chemistry is the focus of the model. Little quantitative work has been done on the influence of heterogeneous chemistry on the composition of the nonurban troposphere.

Most theoretical studies of precipitation scavenging have considered removal of radionuclides generated by atomic bomb testing or the fate of  $\text{SO}_2$  from power plants (e.g., Junge, 1963; Engelmann and Slinn, 1970; Semonin and Beadle, 1974; Hales, 1978). Scavenging of aerosols was the focus of many of these studies. More recent papers have discussed scavenging of gases, particularly  $\text{SO}_2$ , considering factors such as gas transfer to raindrops, the solubility and subsequent chemistry of gases dissolved in clouds and rain, and the intermittent nature of rainfall (Hales, 1972; Adamowicz, 1979; Durham et al., 1981; Schwartz and Frieberg, 1981; Rodhe and Grandell, 1972; Smith, 1981). Nevertheless, even the most recent models of long-range transport of  $\text{SO}_2$  use empirically derived first-order loss coefficients for precipitation scavenging (e.g., Shannon, 1981; Eliassen, 1980). Scavenging of  $\text{HNO}_3$  has been discussed recently by Levine and Schwartz (1982).

Clearly a more quantitative understanding is required of the dynamical, physical, and chemical processes which influence the rate of removal of soluble trace gases throughout the troposphere. This will require an interdisciplinary program of research involving laboratory studies of aqueous-phase chemistry in addition to theoretical analyses and field measurements. More realistic parameterizations of rainout are needed in global multidimensional models, particularly for analysis of the budgets of  $\text{HO}_x$ ,  $\text{NO}_x$ , and sulfur species. Large-scale field measurement campaigns are likely to be an important component of a program investigating the removal of soluble gases, and a great deal of care should go into the design of such experiments. One type of field experiment might involve simultaneous measurements of soluble gas-phase species below and above precipitating clouds and dissolved species in cloud and rain water. However, such a study might

be ill conceived because of the dynamic nature of the atmosphere and the difficulty of finding a sufficiently homogeneous air mass in which to make the measurements. Interpretation of the results of such an experiment might be problematic. Issues such as these need to be addressed in the design of appropriate experiments. Measurements in an area where nonprecipitating clouds are forming and evaporating might answer questions concerning the role of clouds in transporting soluble gases. Tracer experiments involving the release of soluble gases might also be useful. Gatz (1980) reviews investigations of precipitation scavenging of aerosols using chemical tracers.

This rather brief discussion attempts to highlight the need for development of theoretical and experimental programs to investigate the role of heterogeneous removal of soluble gases from the troposphere. This appears to be an area of tropospheric chemistry which would benefit greatly from interaction between theorists and experimentalists in the design of appropriate measurement strategies. Communication among scientists with expertise in gas-phase tropospheric chemistry, aqueous-phase and aerosol chemistry and physics, cloud physics, meteorology, and analytical chemistry will be required to make progress in this complex area.

## *Development of Diagnostic and Prognostic Global Models*

The development and application of this group of models has been described in detail in Seinfeld et al. (1981). They have proven extremely useful in enhancing our understanding of tropospheric chemical processes. Because they have the flexibility to incorporate improved descriptions of physical processes which influence tropospheric chemistry while still retaining the computational simplicity required for the large number of sensitivity studies dictated by the many uncertainties noted earlier, their utility in future investigations is assured.

These models typically employ extensive sets of chemical reactions, while treating transport in an approximate manner. Validation of fast photochemistry is thus of immediate benefit in enhancing the usefulness of these models.

## *Development of 3-D Global Models*

These models have the obvious advantage of promising the most quantitative understanding of the coupling between chemical and physical processes in the troposphere. They describe the relationships between trace species, sources, sinks, and transport at a level of detail not otherwise attainable. The possibility of realistic description of transport of trace species between various tropospheric "composition domains" is a major advantage of this class of models.

Several components are necessary before the modeling can be effective. The sources must be well defined, with magnitudes within a given range; the strength can be varied to test results if it is the only unknown. For ground-level sources, this may require observations of vertical profiles through the boundary layer under stable conditions to emphasize the difference between the boundary layer and the free troposphere. When the suspected source is biospheric, measurements should be made over the various vegetation types, and when it is anthropogenic or oceanic, measurements should be made in appropriate air masses. If the source is thought to be stratospheric, vertical profiles should be taken in locations of suspected entry at what are deemed to be propitious times (e.g., during tropospheric folding events or stratospheric warmings). Correlative measurements such as potential vorticity should be useful at these times. Surface destruction can be investigated through

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observation of boundary layer profiles under stable conditions. Analysis of cloud droplets and rainfall will help quantify heterogeneous processes. It is likely that small-scale modeling of these and other effects will be necessary to develop parameterizations for the sub-grid-scale sources and sinks of global models.

For species whose lifetimes are longer than 1 day, the models must have realistic transports. To examine these transports, observations should be made of passive tracers within a large spatial and temporal domain. Especially important are tracers with well-known sources which are not rained out, such as fluorocarbons or Kr. Simulations of these data can test interhemispheric transport in the models. For processes which involve transport into the troposphere from the stratosphere, the model's capability should be tested with simulations of  $^7\text{Be}$  or atomic debris, such as  $^{90}\text{Sr}$ . Simulations of these downward-moving tracers will also test the parameterization of heterogeneous removal in the model.

Finally, observations are needed of all constituents which could possibly interact with the target species. Every time it is necessary to assume a concentration of a sensitive substance (usually with a uniform distribution) another uncertainty is introduced.

In return, the model will provide the possibility of testing one or a combination of unknowns and will produce distributions which will suggest measurement strategies. A different choice of the unknown(s) will likely alter the model results, particularly in identifying sensitive geographical regions. Further, as the modeling proceeds it will specify which unknowns are most critical for the ultimate distribution, thus helping to determine priorities. Only when models have reached the stage where they can predict concentrations in data-sparse regions and then have these predictions verified will the community feel that the species life cycle is well understood.

The major disadvantage of these models is their heavy computational requirement. It is not presently feasible to include large chemical reaction schemes in 3-D models. Numerous sensitivity studies to determine the effects of parameter uncertainties on model results are also precluded. The validation of model transport using observed tracer distributions is a current priority.

## PROPOSED FIELD MEASUREMENTS

Based on our current understanding of fast photochemistry in the troposphere, three levels of field measurement problems are apparent. First, there are some photochemical problems in which the chemical reaction schemes are thought to be relatively complete and for which reaction rates have been measured. The objective of a field measurement in such cases is to validate (or cast doubt on) the accepted chemical mechanism. Complete sets of constituent measurements required for such validation, along with associated meteorological parameters, may be specified. If some of the required species measurements are impractical, it may be possible to suggest alternate species measurements which would permit calculation of the unknown concentrations. Validation of the chemical mechanism would depend in the latter case on a combination of field measurement and modeling. However, a relatively complete field measurement, designed to address a specific problem in fast photochemistry, can be recommended in these cases. Examples, which will be described further on in this report, include the photochemistry of OH and factors governing the  $\text{NO}_2/\text{NO}$  ratio.



Second, there are problems in which most of the relevant reactions are believed to be known and the rates have been measured, but which clearly still have one or more missing elements. The objectives of a field measurement in such cases are less precise. They would include determining the behavior of the chemical system in a variety of tropospheric domains to permit an assessment of the degree of understanding of the system. Many of the species known to be important in the chemistry of the system can be specified, but there is much less certainty (compared with the first problem class above) that these species measurements will be sufficient to solve the problem. Such field measurements, however, are clearly necessary to understand the system. An example of this class of problem is the partitioning of odd nitrogen among its various forms.

Finally, there are areas of fast photochemistry where little information on reactions and rates is available. Field measurements should be directed towards those parameters which are believed to be the most essential elements in understanding the problem. This may mean measurement of a single species or small groups of species in a variety of tropospheric domains (survey measurements). It is understood at the outset that for this class of problems no single field measurement program can elucidate all the unknowns. Initial data must be obtained which will, in conjunction with model studies, point the way to future, more completely designed measurements. Examples of tropospheric problems in this class are heterogeneous loss, fast photochemistry of sulfur compounds, and halogen chemistry.

Table 6 lists those species involved in fast tropospheric photochemistry for which field measurements are recommended. The assessment column in this table indicates the probability that acquisition of the recommended data will result in solution of the intended problem. The priority rating indicates the importance of solving the problems for global tropospheric chemistry in general.

TABLE 6. FIELD MEASUREMENT RECOMMENDATIONS IN FAST TROPOSPHERIC PHOTOCHEMISTRY

Species/problem	Assessment	Priority
OH	High	1
NO <sub>2</sub> /NO photostationary state	High	1
NO <sub>y</sub> partitioning	Medium	2
CH <sub>3</sub> O <sub>2</sub> (RO <sub>2</sub> )	Medium	2
Halogens	Uncertain	3
Sulfur	Uncertain	2

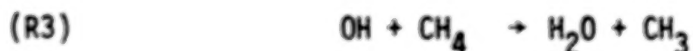
## Fast Photochemistry of OH

The species most involved in tropospheric chemical cycles is the hydroxyl radical. An understanding of its photochemistry is thus central to a more general understanding of tropospheric chemistry, and its measurement should be assigned a high priority.

Primary production of OH occurs as a result of the reaction



The  $O(^1D)$  is produced by ozone photolysis in the 290- to 320-nm region of the ultra-violet spectrum. The primary loss of OH occurs as a result of reaction with CO and  $CH_4$ . The chemistry of OH is complicated by the fact that reactions subsequent to



may generate more OH radicals. This is a consequence of the fact that reactions (R2) and (R3) do not remove odd hydrogen but lead instead to the generation of the peroxy radicals  $HO_2$  and  $CH_2O_2$ , which may then result in OH loss through the formation and removal of peroxides. However, if NO is present in sufficient concentrations its oxidation by peroxy radicals may quickly regenerate OH. These and other factors complicating OH photochemistry are more fully discussed in Appendix A of Seinfeld et al. (1981).

The fact that OH and peroxy radicals may also be produced in the oxidation of NMHC motivates the choice of geographic location. Since more laboratory data are required on reactions and rates for NMHC oxidation, OH measurements should be carried out in regions where NMHC concentrations are expected to be low.

Two sets of species requirements are listed for the OH measurement. In the "ideal experiment," enough species are measured so that the OH model may be validated without recourse to significant assumptions regarding the accuracy of other species calculations. The "minimum set" reflects the necessity of obtaining concentration data on those species most important to primary production and loss of OH and to its regeneration from peroxy radicals.

### I. Hypothesis

The instantaneous OH concentration results from production via  $O(^1D)$  reaction with water vapor, loss (primarily) via reaction with CO and  $CH_4$ , and possible generation during the oxidation of  $CH_4$ , depending on the NO concentration.

### II. Geographic locations

Remote marine and land regions and areas of high anthropogenic emissions; measurements should be conducted over the range of concentrations characteristic of different tropospheric regimes (e.g., low NMHC/remote marine to high NMHC/urban)

### III. Measurement requirements



## A. Species

1. Ideal experiment: OH; H<sub>2</sub>O, O<sub>3</sub>, CH<sub>4</sub>, CO, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, NO, H<sub>2</sub>CO, CH<sub>3</sub>OOH, NMHC
2. Minimum set: OH; H<sub>2</sub>O, O<sub>3</sub>, CH<sub>4</sub>, CO, NO

## B. Spatial - *in situ* (point)

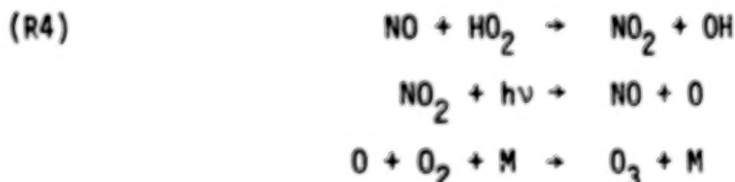
- C. Temporal - 1 second; may be relaxed to longer times if effects of concentration fluctuations can be determined

## D. Meteorology

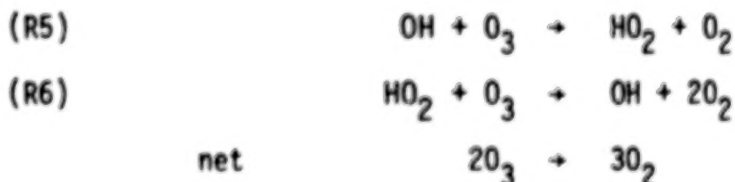
1. Temperature
2. Pressure
3. Solar flux (290 to 320 nm with 1-nm resolution)

### Fast Photochemistry of HO<sub>2</sub>

There are as yet no measurements of the hydroperoxy radical, HO<sub>2</sub>, in the troposphere. Model calculations indicate that it should be present in concentration greater than about 10<sup>8</sup> molecules cm<sup>-3</sup>. It is believed that HO<sub>2</sub> plays a major role in both the chemical production and loss of ozone in the troposphere. Production of ozone follows the oxidation of NO to NO<sub>2</sub>:



while destruction occurs via the catalytic cycle



The production of NO<sub>2</sub> from NO is also an essential step in the production of nitric acid and organic nitrates.

HO<sub>2</sub> is produced by reaction (R5) as well as in reactions following the oxidation of CH<sub>4</sub> by OH. Loss of HO<sub>2</sub> occurs through reactions with CH<sub>3</sub>O<sub>2</sub>, OH, NO, and O<sub>3</sub>, though it may be regenerated subsequent to some of these losses.

### I. Hypothesis

The instantaneous HO<sub>2</sub> concentration results from reactions following the oxidation of CO and methane. It is destroyed in reactions forming peroxides and in reaction with OH, NO, and O<sub>3</sub>.

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## II. Geographic location

Remote marine regions (low NMHC concentrations required)

## III. Measurement requirements

A. Species:  $\text{HO}_2$ ;  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{O}_3$ ,  $\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CH}_3\text{O}_2$ ,  $\text{H}_2\text{CO}$ ,  $\text{NO}$ , NMHC

B. Spatial - *in situ* (point)

C. Temporal - same as OH

D. Meteorology

1. Temperature

2. Solar flux (290 to 360 nm with 10-nm resolution)

### *Fast Photochemistry of $\text{CH}_3\text{O}_2$*

The chemistry of the methylperoxy radical is similar to that of  $\text{HO}_2$ . There are as yet no measurements of  $\text{CH}_3\text{O}_2$  in the troposphere and models indicate an expected abundance greater than or equal to  $10^8$  molecules  $\text{cm}^{-3}$ . Methylperoxy is potentially important in the production of tropospheric ozone and other processes following from the oxidation of  $\text{NO}$  to  $\text{NO}_2$ .

$\text{CH}_3\text{O}_2$  is produced in the oxidation of methane by OH and is removed via reaction with  $\text{NO}$  and  $\text{HO}_2$ . Formation of methyl hydrogen peroxide may to some degree serve as a reservoir for  $\text{CH}_3\text{O}_2$ . Other reactions subsequent to "loss" reactions cited above may result in further  $\text{CH}_3\text{O}_2$  production, but only via the methane oxidation route. This is, therefore, not a complicating factor in validating the fast photochemistry of  $\text{CH}_3\text{O}_2$ .

### I. Hypothesis

In the absence of information concerning contributions from NMHC's,  $\text{CH}_3\text{O}_2$  is produced in the oxidation of methane and lost in reactions with  $\text{NO}$  and  $\text{HO}_2$ .

## II. Geographic location

Remote marine (low NMHC required)

## III. Measurement requirements

A. Species:  $\text{CH}_3\text{O}_2$ ;  $\text{CH}_4$ ,  $\text{CH}_3\text{OOH}$ ,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{NO}$ , NMHC

B. Spatial resolution - *in situ* (point)

C. Temporal resolution - 1 second

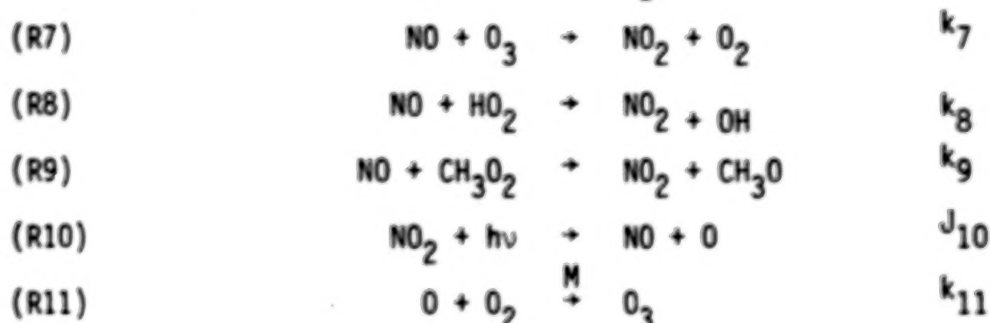
D. Meteorology

1. Temperature

## 2. Solar flux (290 to 350 nm with 10-nm resolution)

### *NO<sub>2</sub>/NO Photostationary State*

Among the most important reactions in the tropospheric odd-nitrogen budget are those which rapidly interconvert NO and NO<sub>2</sub>:



If reaction (R7) is much more important than reactions (R8) and (R9) in oxidizing NO, then the ratio of NO<sub>2</sub> to NO is determined solely by the ozone concentration and the rates of reactions (R7) and (R10) (Leighton, 1961):

$$[\text{NO}_2]/[\text{NO}] = \frac{k_7}{J_{10}} [\text{O}_3] \quad (4)$$

Reaction (R7) competes with oxidation by peroxy radicals (reactions (R8) and (R9)), which may be written generally as:



If this is important in converting NO to NO<sub>2</sub>, then operation (4) must be modified to:

$$[\text{NO}_2]/[\text{NO}] = \frac{k_7[\text{O}_3] + k_{12}[\text{RO}_2]}{J_{10}} \quad (5)$$

Recent measurements of the ratio [NO<sub>2</sub>]/[NO] were carried out by Kelly et al. (1980) in clean air with the result that deviations from equation (4) by factors of 3 to 7 were observed. Since there are as yet no tropospheric measurements of RO<sub>2</sub>, equation (5) remains a hypothesis. Simultaneous measurements of RO<sub>2</sub> and the other concentrations entering equation (5) are required to test our understanding of this important photochemical mechanism.

### I. Hypothesis

The NO<sub>2</sub>/NO ratio is determined by reactions (R7) to (R11) and may be calculated from equation (5).

### II. Geographic location

Remote marine and remote continental areas (it is desirable to test equation (5) under different circumstances)

### III. Measurement requirements

- A. Species:  $\text{NO}$ ,  $\text{NO}_2$ ;  $\text{O}_3$ ,  $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2$
- B. Spatial - *in situ* (point)
- C. Temporal - 1 minute
- D. Meteorology
  - 1. Temperature
  - 2. Solar flux (290 to 500 nm with 10-nm resolution)

### $\text{NO}_y$ Partitioning

The principal forms of odd nitrogen in the troposphere are expected to be  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ ,  $\text{HO}_2\text{NO}_2$ , and PAN. PAN represents a group of organic nitrates having the chemical formula  $\text{RC(O)O}_2\text{NO}_2$  where R is an acetyl group. Current problems related to the partitioning of  $\text{NO}_y$  include the following:

1. Observations of  $\text{NO}_3$  during the night in Colorado mountain air indicate a loss of  $\text{NO}_3$  which is not accounted for by current understanding of odd-nitrogen chemistry (Noxon et al., 1980).
2. Observations of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) and  $\text{HNO}_3$  at Niwot Ridge, Colorado (Kelly et al., 1980) show  $\text{HNO}_3$  concentrations always less than  $\text{NO}_x$ . This contrasts with current model results indicating that  $\text{HNO}_3$  is the dominant form of  $\text{NO}_y$  in remote or relatively clean tropospheric air masses.
3. The role of organic nitrates has not generally been considered in studies of unpolluted tropospheric air. However, the relatively long lifetime of PAN's in the middle and upper troposphere could lead to their transport to remote locations and influence the local  $\text{NO}$  chemistry (Crutzen, 1979). Model calculations (Singh and Hanst, 1981; Brewer et al., 1982) indicate a potential role for PAN in the remote troposphere.

Generally, it is desirable to measure  $\text{NO}_x$  components and related species in a variety of characteristic tropospheric composition domains. It is not known, for example, whether the scavenging of  $\text{NO}_3$  at night is a peculiarity of the continental (Colorado mountain) location at which it was observed or whether this might be a more general phenomenon.

The partitioning of odd nitrogen involves reactions between  $\text{NO}_y$  components and the other major chemical groups in the troposphere - odd oxygen, odd hydrogen, and methane oxidation products. Heterogeneous processes are responsible for odd-nitrogen removal. Physical sources and sinks and possibly stratosphere-troposphere exchange play a role in the  $\text{NO}_y$  budget. Though the field measurements specifications listed below may not include all the observations needed for a resolution of the odd-nitrogen partitioning problem, they do include those chemical elements currently believed to be important. They will provide a much more complete data set for theoretical studies than is currently available.



## I. Hypothesis

Odd nitrogen is introduced in the troposphere by physical and biological processes whose characteristics vary with the region being considered. It is partitioned in its various forms by chemical interaction with  $O_x$ ,  $HO_x$ , and methane oxidation products ( $CH_3O_2$ ). It is removed by rainout of  $HNO_3$ , possibly by surface deposition, and by as yet unidentified chemistry.

## II. Geographic location

Various locations characteristic of different "composition domains" are desirable, for example:

- A. Remote marine (boundary layer and free troposphere)
- B. Remote continental (boundary layer and free troposphere)

## III. Measurement requirements

### A. Species

1. Ideal experiment:  $NO$ ,  $NO_2$ ,  $NO_3$ ,  $HNO_3$ ,  $PAN$ ,  $H_2O$ ,  $OH$ ,  $HO_2$ ,  $CH_3O_2$ ,  $O_3$ , NMHC

2. Minimum set:  $NO$ ,  $NO_2$ ,  $NO_3$ ,  $HNO_3$ ,  $PAN$ ,  $H_2O$ ,  $O_3$ , NMHC

### B. Spatial - *in situ* (point)

### C. Temporal - 1 minute

### D. Meteorology

1. Temperature

2. Pressure

3. Solar flux (290 to 500 nm with 10-nm resolution)

## *Fast Photochemistry of Sulfur*

Because the oxidation of  $SO_2$  to  $H_2SO_4$  can often have a significant impact upon the acidity of precipitation, the development of a comprehensive understanding of the cycle of atmospheric sulfur is a major goal of the NASA tropospheric program planning (Seinfeld et al., 1981). A schematic representation of our present view of this cycle is illustrated in figure 4. Note that the oxidation of reduced sulfur compounds such as  $H_2S$ ,  $CH_3SCH_3$ ,  $CS_2$ , and others is believed to lead to the production of  $SO$  via multistep reaction sequences (Friend, 1973; Granat et al., 1976).  $SO_2$  is in turn oxidized, probably by a combination of homogeneous and heterogeneous reactions (Davis et al., 1979; Penkett et al., 1979a; Calvert et al., 1978), and is ultimately converted to  $H_2SO_4$ , which is removed in precipitation. It now appears that  $OCS$  is relatively inert in the troposphere and is primarily destroyed in the stratosphere, where it may be a major precursor to the stratospheric sulfate layer (Crutzen, 1976).

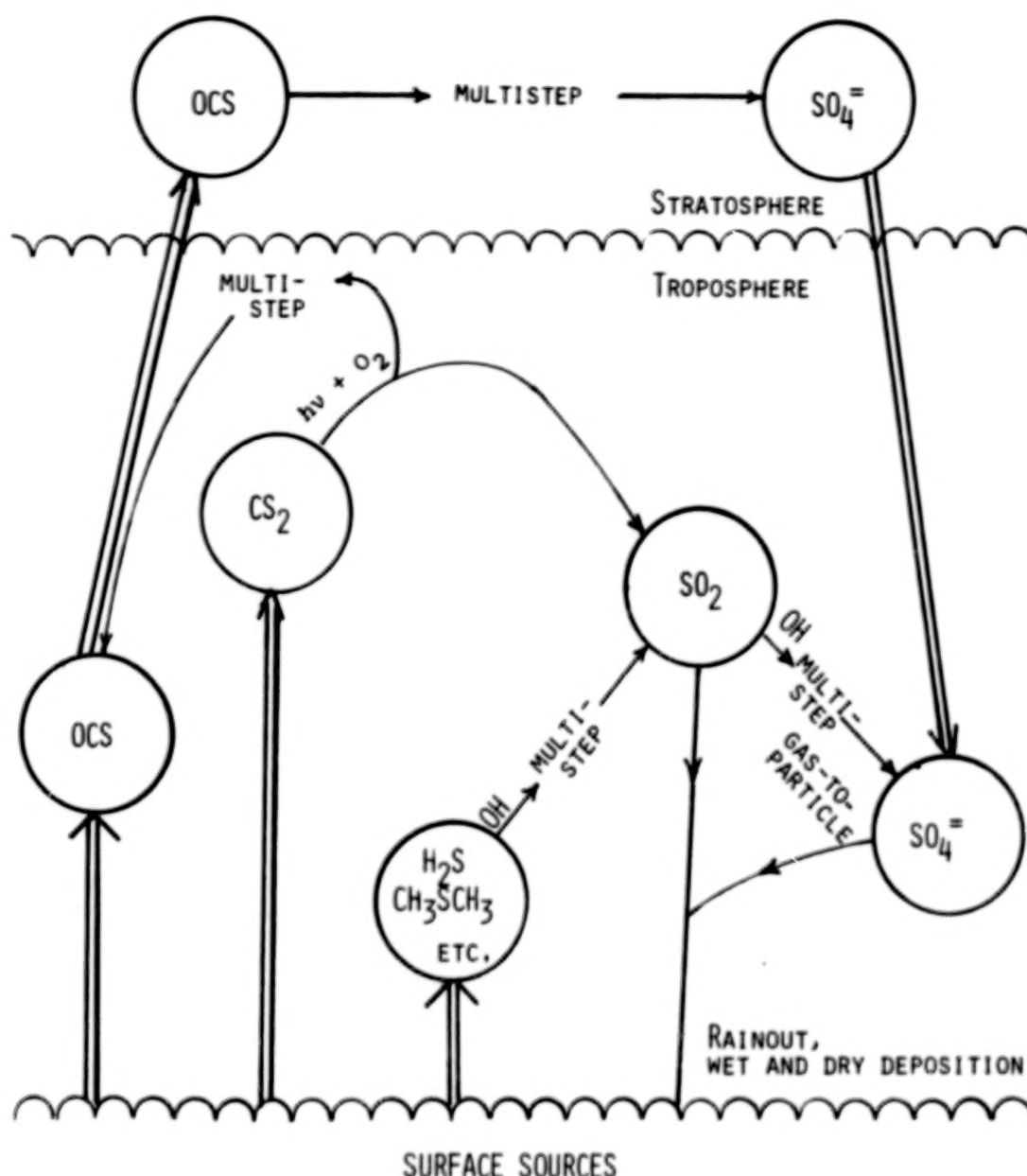


Figure 4. A tentative scheme for the oxidation and removal of atmospheric sulfur species.

In terms of experiments to elucidate the fast photochemistry of this system, measurement schemes will be needed to verify the chemical pathways by which reduced sulfur species are oxidized to  $\text{SO}_2$  and  $\text{SO}_2$  is oxidized to  $\text{SO}_4$ . It is probable that it will be useful to carry out these experiments in a variety of different environments, including areas of intense S emissions (i.e., swamps, tidal flats, marshes) as well as less active regions such as remote oligotrophic marine areas. Unfortunately, our present understanding of the distributions of atmospheric sulfur species and the elementary chemical reactions involved in the previously described oxidation chains is quite poor. In addition, the instrumentation necessary to measure many of the key atmospheric constituents has yet to be developed. For these reasons, the highest priority items for the study of the sulfur system should be survey measurements, studies of surface source strengths, laboratory

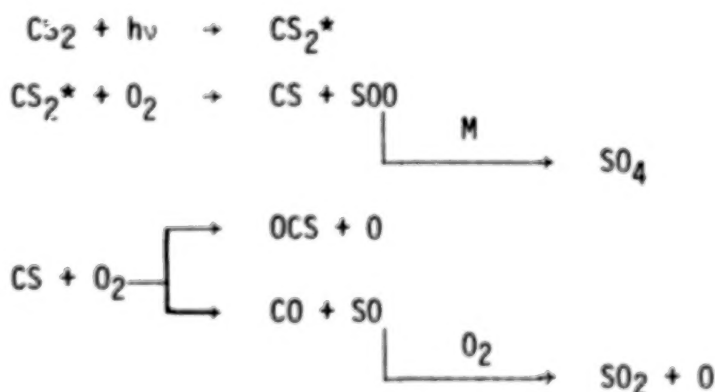
kinetic studies coupled with photochemical modeling exercises, and technology development. Once these tasks are completed it will be possible to design specific fast photochemistry experiments to selectively study various facets of the atmospheric S system. To indicate what types of experiments might prove useful, a few highly tentative measurement schemes are presented below.

In the case of  $H_2S$  oxidation, for instance, it is believed that oxidation is initiated by reaction with OH, i.e.,



and is followed by an as yet unconfirmed reaction sequence which produces  $SO_2$  as an end product. If the necessary technology could be developed, it may prove useful to simultaneously measure levels of  $H_2S$ , HS, possibly another intermediate of the  $H_2S$  oxidation chain, and OH, as well as  $SO_2$ . A similar experiment for  $CH_3SCH_3$  may also prove to be informative.

A possible oxidation sequence for  $CS_2$  (Wood and Heicklen, 1971; Wine et al., 1981) involves



If laboratory studies should ultimately verify that this is a viable reaction scheme, a potential fast-photochemistry experiment would be to simultaneously measure  $CS_2$ , solar flux ( $300 \text{ nm} \leq \lambda \leq 360 \text{ nm}$ ), CS, and  $SO_2$ . However, according to model calculations, if CS is formed as indicated in this reaction sequence then its concentration could be as low as  $10^3 \text{ molecules cm}^{-3}$ . Thus it is conceivable that such an experiment would require a substantial advance in our technological capabilities.

In the case of  $SO_2$  oxidation it may prove necessary to measure species in the liquid/solid phase as well as the gas phase to properly study the chemical pathway from  $SO_2$  to  $SO_4$ . Here, especially, survey measurements of  $SO_2$  and S in aerosols and clouds, as well as laboratory studies of  $SO_4$  oxidation, are needed before an appropriate fast photochemistry experiment can be designed. It is also perhaps relevant to note here that recent measurements by Maroulis et al. (1980) indicate the presence of a significant free tropospheric source of  $SO_2$  in the remote marine atmosphere. Experiments designed to determine the precursor compounds which lead to this source as well as its chemical mechanism must be considered if subsequent  $SO_2$  observations confirm the earlier findings of Maroulis and coworkers.

In summary we find that while the fast-photochemistry sulfur experiments will be an important part of the tropospheric program, we do not yet have enough

information to design specific measurement strategies. For the short term, therefore, survey measurements, laboratory measurements coupled with modeling studies, and technology development should be pursued in this area.

## I. Hypothesis

Sulfur compounds may have a widespread and significant impact on the acidity of precipitation. They are emitted into the atmosphere in reduced forms of  $\text{SO}_2$ . Reduced sulfur is converted to  $\text{SO}_2$  by gas-phase photochemistry.  $\text{SO}_2$  is converted to  $\text{H}_2\text{SO}_4$  by gas-phase and/or heterogeneous processes.

## II. Geographic location

Survey measurements at various locations, such as swamps, tidal flats, near volcanoes, oceanic regions, and in the boundary layer and free troposphere

## III. Measurement requirements

A. Species:  $\text{H}_2\text{S}$ ,  $(\text{CH}_3)_2\text{S}_2$ ,  $(\text{CH}_3)_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{CS}_2$ , OH

B. Spatial - *in situ*

C. Temporal - 1 minute

D. Meteorology

1. Temperature

### *Fast Photochemistry of Halogen Species*

It is now recognized that chlorine and bromine compounds (i.e., ClX and BrX) can play an important role in the chemistry of the stratosphere; however, their importance to the tropospheric photochemistry has not yet been firmly established (Cicerone, 1981). Significant quantities of inorganic bromine and chlorine compounds may be present in the troposphere. (For example, lower tropospheric HCl concentration measurements on the order of 1 ppbv have been reported by Junge (1957), Duce (1969), Chesselet et al. (1972), Farmer et al. (1976), and others.) However, present-day photochemical models indicate that virtually all of the tropospheric ClX and BrX is tied up in essentially inert forms such as HCl, HOCl, ClONO<sub>2</sub>, HBr, HOBr, and BrONO<sub>2</sub>. As a result, at this time the fast photochemistry of ClX and BrX in the troposphere does not appear to be a high-priority item for the tropospheric program. Nevertheless, it would be advisable to conduct survey measurements of tropospheric ClX and BrX compounds. Should these measurements and/or refinements in our understanding of ClX and BrX kinetics indicate that these compounds are photochemically active in the troposphere, it is conceivable that a fast photochemical experiment centering on ClO and/or BrO may be of value.

While ClX and BrX do not appear to be photochemically active in the troposphere, recent calculations by Chameides and Davis (1980) indicate that inorganic iodine (IX) is probably highly reactive in the troposphere. A tentative scheme for tropospheric IX photochemistry is illustrated in figure 5. This figure shows the IX system to be highly cyclic with I atoms being a main cycling point. While many



of these chemical cycles have no net effect upon the tropospheric system, there are others which can have a net chemical impact. For example, the reaction sequence of

followed by



or



followed by



acts catalytically to destroy ozone. While many kinetic uncertainties exist in the system, Chameides and Davis estimate that in regions where total IX concentrations approach 10 pptv or greater, iodine may have a significant impact upon the tropospheric  $O_3/H_2O_2$  system. It is therefore recommended that if survey measurements indicate that these concentration levels of IX do occur in the troposphere, then a fast photochemical measurement scheme involving simultaneous observation of IO, HOI,  $O_3$ , OH, and, if possible, also  $HO_2$  may prove to be quite important to verifying our understanding of this system. In addition, simultaneous nighttime measurements of IO,  $NO_2$ , and  $IONO_2$  may also be valuable. In each case, these measurements should be carried out in regions of significant IX levels and varying levels of aerosols and moisture. Temporal resolution should ideally be on the order of a few seconds, although integration times ranging up to 1 hour may prove to be acceptable.

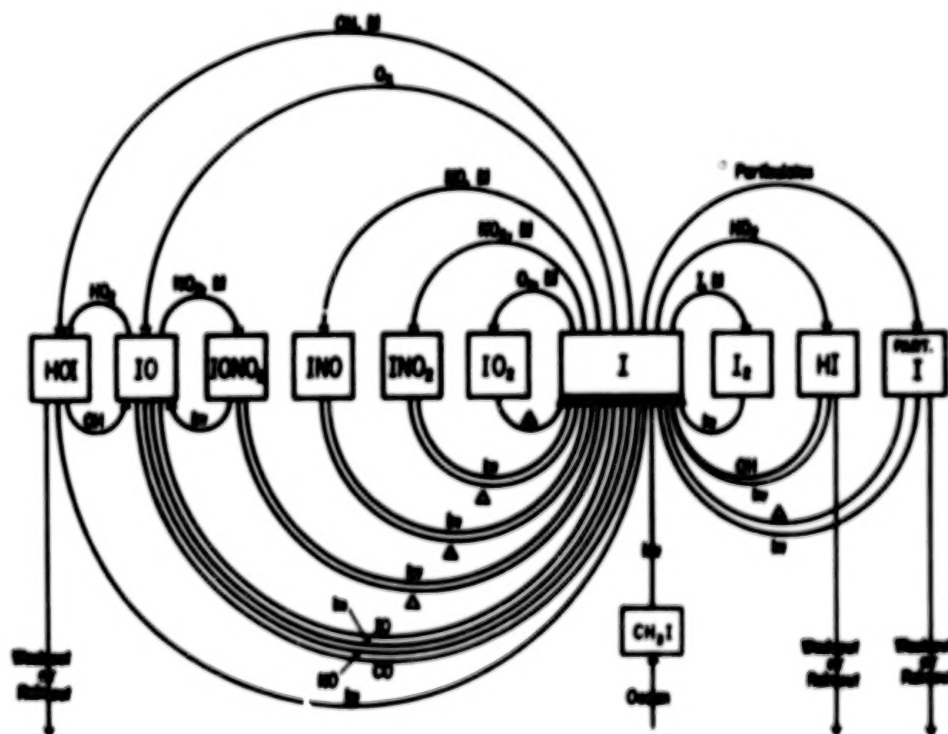


Figure 5. Tropospheric iodine photochemistry. (From Chameides and Davis, 1980.)

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## I. Hypothesis

IX is (or is not) present in the troposphere in concentrations of approximately 10 pptv or greater.

## II. Geographic location

Remote marine boundary layer

## III. Measurement requirements

A. Species: IO, HOI, CH<sub>3</sub>I

B. Spatial - *in situ*

C. Temporal - < 10 seconds (for IO, HOI)

D. Meteorology

1. Temperature

2. Solar flux (290 to 340 nm with 10-nm resolution)

LONG-TERM MONITORING TO UNDERSTAND TROPOSPHERIC VARIABILITY

## SCIENTIFIC BACKGROUND AND ISSUES

It has become clear in recent years that human activities are having a measurable effect on certain global geochemical cycles. The most obvious and well-documented impact on the global troposphere is the increased concentration of carbon dioxide related to fossil fuel combustion and possibly affected by other human activities such as forest clearing (Machta et al., 1977; Pearman, 1978). Several more recent data sets show that background concentrations of other trace gases ( $\text{N}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{O}_3$ ) may be increasing, as discussed subsequently. Geochemical calculations suggest that anthropogenic fluxes of volatile trace elements such as arsenic, selenium, and mercury may also be sufficient to impact global tropospheric air quality (Lantzy and Mackenzie, 1979; Nriagu, 1979).

Craig et al. (1976) suggested that the concentration of  $\text{N}_2\text{O}$  increased at a rate of 0.5 ppb per year from 1961 to 1974, based on an analysis of stored air samples. A similar rate of increase (about 0.2 percent per year) was found for the period from 1976 to 1980 from measurements of  $\text{N}_2\text{O}$  at NOAA-GMCC (Geophysical Monitoring for Climate Change) stations in Alaska, Hawaii, and the South Pole (Weiss, 1981).

Rasmussen and Khalil (1981a) have monitored the concentration of  $\text{CH}_4$  in Oregon since early 1979 and find an increase of 2 percent per year for the first 2 years of data. Sporadic measurements of  $\text{CH}_4$  have been made by several investigators at various locations since 1965. It is unclear whether  $\text{CH}_4$  has been increasing since then (as some have suggested) because of problems associated with long-term maintenance of calibration standards (Heidt and Ehhalt, 1980) and systematic differences in absolute concentrations reported by different laboratories. The recent results of Rasmussen and Khalil also indicate that  $\text{CH}_4$  may vary seasonally.

Carbon monoxide has been monitored on Hawaii since 1975, and routine measurements are being made at Capetown ( $35^\circ\text{S}$ ) (Seiler and Fishman, 1981); however, most of these data have not been published. Results from both locations indicate that CO apparently varies seasonally, with lowest values in late summer. The data base is insufficient to determine if concentrations are increasing with time (Seiler, 1979).

Surface ozone has been measured at the NOAA-GMCC stations mentioned previously since 1973 and at Somoa since 1976 (Oltmans, 1981). No trends are evident in these data, although it has been suggested that tropospheric ozone is increasing in the Northern Hemisphere, based on analysis of ozonesonde measurements from altitudes of 2 to 8 km (Hudson and Reed, 1979).

All of the above gases have sources which may be impacted by man's industrial and agricultural activities. The magnitude and potential effects of global scale changes in the concentrations of these gases are in the preliminary stages of investigation. It is clearly vital that high quality monitoring programs be established so that man's impact on global air quality may be assessed in the future. The current ambiguous data record for  $\text{CH}_4$  should serve as a warning to those ambivalent about the usefulness of long-term monitoring programs, while measurements of  $\text{CO}_2$  since 1957 should demonstrate the value of such a program.

Development of a monitoring strategy for tropospheric air quality should draw on experience gained from two existing programs oriented towards stratospheric chemistry. The NOAA Geophysical Monitoring for Climate Change (GMCC) program and the Chlorofluorocarbon Monitoring Program (sponsored by the Chemical Manufacturers Association, CMA) have monitored concentrations of  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  at remote locations since 1977 and 1978, respectively. (See, e.g., National Oceanic and Atmospheric Administration, 1979; Black et al., 1981.) Methyl chloroform has been monitored at a variety of locations since 1979 (Rasmussen and Khalil, 1981b). Concentrations of the halocarbons are increasing as a result of man-made emissions. Measurements from 1970-1980 (other than those described above) are reviewed by Logan et al. (1981). Data for  $\text{CH}_3\text{CCl}_3$  are particularly important in the context of tropospheric chemistry, since analysis of the budget for  $\text{CH}_3\text{CCl}_3$  provides a useful test of global models for OH. Data for  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  provide useful tests of the transport parameterizations in 2- and 3-D tropospheric and stratospheric models.

The only systematic long-term global tropospheric air quality monitoring efforts presently active are associated with the National Oceanic and Atmospheric Administration Program on Geophysical Monitoring for Climatic Change and the World Meteorological Organization's (WMO) network for monitoring background air pollution (BAPMON). So far, the WMO-BAPMON program has a total of 109 stations operating in 41 countries (figure 6), with possible expansion to 200 stations in 70 countries in the future (Wallen, 1980). While this network is impressive in the number of stations, the number of air quality parameters monitored is very limited and quality control is badly needed. The only reliable long-term global tropospheric data set is carbon dioxide.

Questions which need to be addressed relative to long-term monitoring needed to understand global tropospheric processes include the following.

- Assuming that chemical species identified by current research as high priority for long-term global monitoring (i.e.,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ , Pb, Hg, and selected halocarbons) can be quantitatively monitored at remote locations, what criteria should be used to establish the spatial and temporal sampling requirements for a monitoring program?
- What type of trend analysis techniques will be used to analyze the global network data, and what constraints do the analytical techniques place on the sampling program?
- What type of meteorological data base is needed to enhance the analysis of long-term chemical data sets?

## PROPOSED RESEARCH

It is premature to issue highly specific design criteria for a global tropospheric air quality monitoring system. The following recommendations are directed to near-term problems of determining a strategy for large-scale long-term tropospheric monitoring.

- A workshop on the design of long-term monitoring of the global troposphere should be convened to review existing experience and research results. Special attention should be given to experience gained by the existing NOAA, WMO, and CMA programs.



- Two general research approaches to seeking optimal strategies for monitoring system network design should include statistical methods (Tiao et al., 1975; Hill and Sheldon, 1975; Karol et al., 1976) and modeling studies (Moxim and Mahlman, 1980). Theoretical studies should be directed to the question of whether an already operating network can be upgraded or whether new stations are necessary.
- Specific research efforts on atmospheric chemical monitoring at remote locations (e.g., Rasmussen and Khalil, 1981a, b; Duce et al., 1980; Cunningham and Zoller, 1981) should be continued with emphasis on establishing a research data set for network design.

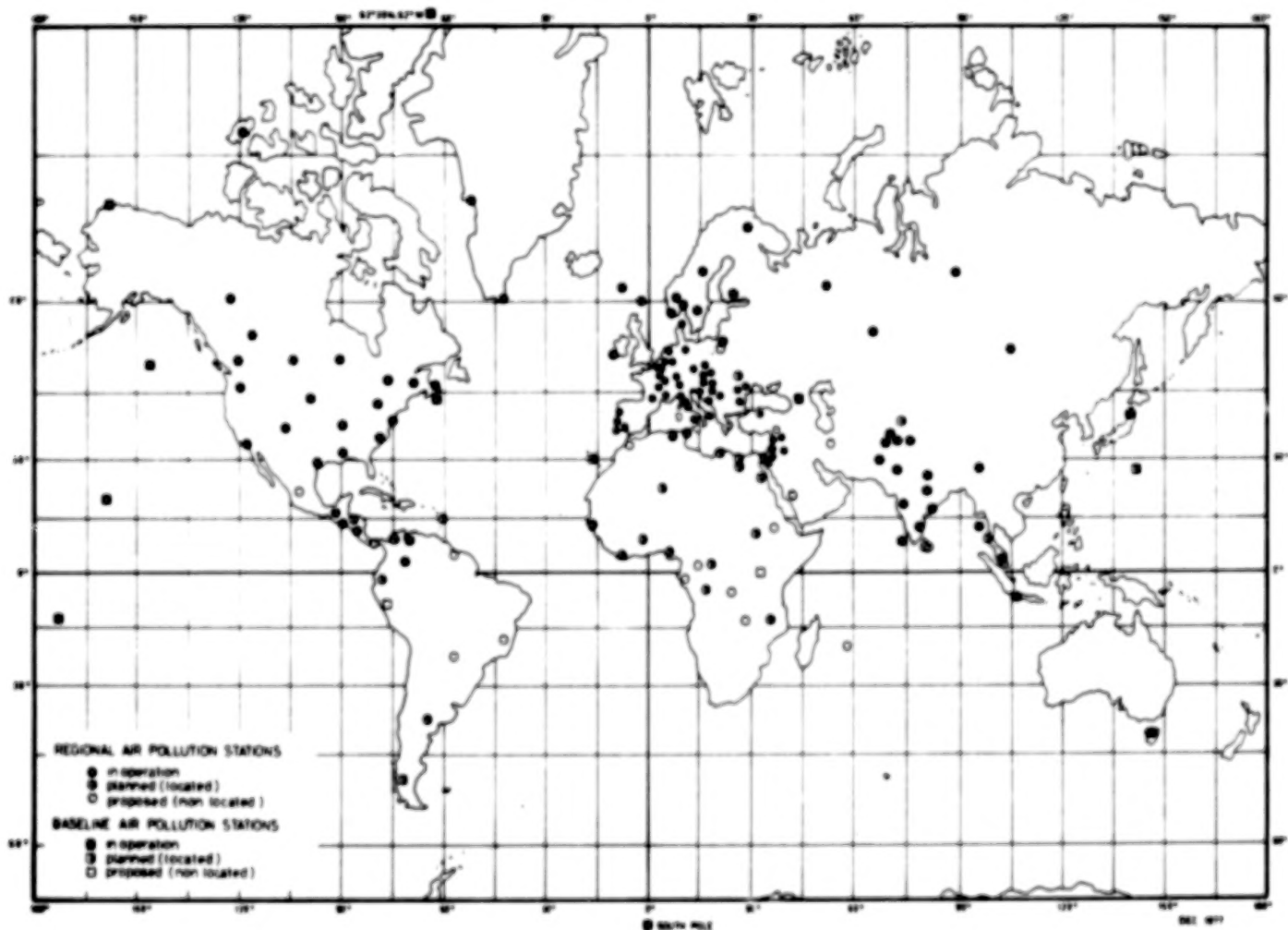


Figure 6. Present state of World Meteorological Organization network for monitoring background air pollution.  
(From Sors, 1980.)

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## APPENDIX A

### ATTENDEES

Mr. Richard J. Bendura  
NASA Langley Research Center

Dr. Gregory R. Carmichael  
University of Iowa

Dr. Richard A. Carrigan  
National Science Foundation

Dr. William L. Chameides  
Georgia Institute of Technology

Dr. K. Roland Chan  
NASA Headquarters

Dr. Sushil Chandra  
NASA Goddard Space Flight Center

Dr. Ralph J. Cicerone  
National Center for Atmospheric  
Research

Mr. Howard J. Curfman, Jr.  
The Bionetics Corporation

Dr. Edwin F. Danielsen  
NASA Ames Research Center

Dr. Jack Fishman  
NASA Langley Research Center

Dr. James E. Hansen  
Goddard Institute for Space Studies

Dr. Robert C. Harriss  
NASA Langley Research Center

Dr. R. J. Lantzy  
Exxon Research & Engineering Co.

Dr. James D. Lawrence  
NASA Langley Research Center

Dr. Donald H. Lenschow  
National Center for Atmospheric  
Research

Dr. Shaw C. Liu  
National Oceanic & Atmospheric  
Administration

Dr. Jennifer A. Logan  
Harvard University

Dr. Michael B. McElroy  
Harvard University

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Mr. John P. Mugler, Jr.  
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Dr. Leonard K. Peters  
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Dr. Henry G. Reichle, Jr.  
NASA Langley Research Center

Dr. David Rind  
Goddard Institute for Space Studies

Dr. Richard W. Stewart  
NASA Goddard Space Flight Center

Dr. Richard S. Stolarski  
NASA Goddard Space Flight Center

Dr. John T. Suttles  
NASA Headquarters

Dr. Giorgio Tesi  
National Science Foundation

Dr. Owen B. Toon  
NASA Ames Research Center

Dr. Robert T. Watson  
NASA Headquarters

APPENDIX BMODELING STUDIES CURRENTLY SUPPORTED BYNASA TROPOSPHERIC AIR QUALITY PROGRAM

**TITLE:** GLOBAL TROPOSPHERIC BUDGET MODELING

**P.I.:** Dr. Richard W. Stewart  
NASA Goddard Space Flight Center

**STATUS:** First year of 3-year continuation proposal approved in FY 1981

**BRIEF DESCRIPTION OF MODELING:**

*Current Model Development*

Previous research carried out under this tropospheric modeling program has been concerned with the utilization of simplified models to study the global-scale budgets of ozone, carbon monoxide, and nitrogen and to investigate potential consequences of human activity on the chemistry of the troposphere. The first models used in these studies were box models designed to determine if observed background levels of trace species were consistent with the available chemical data base and with independent estimates of physical and biological sources and sinks of various constituents (Stewart et al., 1977a, b). Recently a latitude-dependent model for the vertically and zonally averaged annual mean distributions of trace species was developed. This is utilized in studying the relationships between the observed meridional structure of various species distributions and the physical separation of sources and sinks in different latitude belts. The formulation of this model represents an extension of the model of Czeplak and Junge (1974) to consideration of the case of chemically interacting species. The models indicated above have been applied to studies of the budgets of the tropospheric carbon/nitrogen/ozone system.

*Proposed Model Extensions and Improvements*

In addition to the further application of existing models to study the problems of trace species distributions in the troposphere, this task envisions the following model development activities:

1. Addition of time-dependence to the current one-dimensional (latitude) model
2. Extension of the latitude-dependent model to two dimensions (latitude and longitude)
3. Coupling the energy balance climate model developed at the State University of New York (SUNY) at Stony Brook to the existing latitude-dependent model and its time-dependent version (1. above)
4. Theoretical investigation of the effects of physical processes on the budgets of tropospheric species; emphasis will be on development of a

coupled gas/liquid-phase chemistry and the effects of wet deposition, and on the influence of boundary layer transport and chemistry on the budget of the global troposphere and the stratosphere

**TITLE:** AN EXAMINATION OF BOUNDARY LAYER AND TRANSPORT EFFECTS ON GLOBAL TROPOSPHERIC TRACE GAS MEASUREMENTS AND BUDGET CALCULATIONS

**P.I.:** Dr. Jack Fishman  
NASA Langley Research Center

**STATUS:** First year of 3-year new proposal approved in FY 1981

**BRIEF DESCRIPTION OF MODELING:**

Several research tasks will be addressed during the initial phases of the proposed research period. These include:

1. A numerical investigation of the dynamics of the planetary boundary layer so that a realistic parameterization of the exchange processes between the boundary layer and free troposphere can be developed; this parameterization will be tested on existing data sets and applied to existing global models of tropospheric trace gases (e.g., Fishman et al., 1979b) to provide insights into how such a lower boundary condition affects the interpretation of the global cycles of CO, NO<sub>x</sub>, tropospheric ozone, and other trace constituents
2. The development of a synoptic-scale isentropic trajectory package which will be used to support the analyses of trace gas measurements
3. The refinement of a numerical scheme which will better simulate the chemistry within the planetary boundary layer

**TITLE:** COUPLING OF THE SO<sub>x</sub> and NO<sub>x</sub> CYCLES IN THE TROPOSPHERE: THREE-DIMENSIONAL TRANSPORT/CHEMISTRY/REMOVAL ANALYSIS

**P.I.:** Dr. Gregory R. Carmichael  
Chemical and Materials Engineering Program  
University of Iowa

**STATUS:** Second year of 3-year proposal approved in FY 1981



## BRIEF DESCRIPTION OF MODELING:

Research to improve our understanding of the tropospheric  $\text{SO}_x$  and  $\text{NO}_x$  pollutant cycles is being conducted. This research is extending development of a 3-dimensional transport/chemistry/removal model for  $\text{SO}_x$  and  $\text{NO}_x$  so that it can be used in conjunction with observational data such as those obtained via remote sensing from orbiting platforms. The initial phase of this study entails the extension and improvement of a recently developed 3-dimensional  $\text{SO}_x$  transport model to include the  $\text{NO}_x$  transport equations and to extend and incorporate a submodel for the simultaneous wet removal of  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{HNO}_x$ , and  $\text{HCl}$ . In latter phases, the  $\text{SO}_x$  and  $\text{NO}_x$  model will be used to investigate the tropospheric cycles of these trace species and will be interfaced with other tropospheric models to study the interactions between  $\text{SO}_x$ - $\text{NO}_x$  and the  $\text{CH}_4$ - $\text{CO}$ ,  $\text{O}_3$ ,  $\text{NH}_3$  models.

A 3-dimensional  $\text{SO}_x$  transport model has been developed on the NASA LaRC CDC STAR computer. It is a grid model incorporating the following significant features:

1. Incorporates gas-phase and heterogeneous chemistry diurnally; this includes reaction schemes to photochemically generate  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{H}_2\text{O}_2$ , and other radical concentrations
2. Mixing layer development and dissipation which enables emissions above the layer with possible subsequent entrainment later in the day and vice versa (i.e., emissions within the mixing layer may also be transported aloft)
3. Spatially and temporally varying wind, temperature, water vapor, and eddy diffusivity fields
4. Incorporates removal of  $\text{SO}_2$  and sulfate at ground level; the deposition velocity is parameterized to depend on meteorological conditions, land-use type, and surface roughness
5. Can readily incorporate other phenomena, such as  $\text{NO}_x$  transport and gaseous and particulate washout during precipitation

TITLE: THE PHOTOCHEMISTRY OF TROPOSPHERIC  $\text{CO}$  AND  $\text{NO}_x$  AND THE IMPACT OF ANTHROPOGENIC EMISSIONS

P.I.: Dr. William L. Chameides  
Georgia Institute of Technology

STATUS Second year of 3-year continuation proposal approved in FY 1981

# BEST DOCUMENT AVAILABLE

## BRIEF DESCRIPTION OF MODELING:

We are presently using three basic models in our studies: a simple time-dependent box model for studying chemical interactions; a one-dimensional model, as described by Chameides and Stedman (1977) and Chameides (1978); and a two-dimensional, diagnostic model for short-lived species, similar to that of Wofsy (1976) and Crutzen and Fishman (1977). We are also currently developing a multiple box model for simulating the global photochemistry via several coupled boxes, each representing a specific region of the globe. Furthermore, via collaborative studies with D. Butler and R. S. Stolarski, we will be able to study tropospheric-stratospheric coupling with the NASA Goddard stratospheric photochemical models.

The one-dimensional model couples photochemistry and vertical transport using the usual eddy diffusion coefficient parameterization. In this model the vertical distributions of all species of interest are calculated, in the steady state or as functions of time, with appropriate boundary conditions or an assumed photochemical equilibrium. Globally averaged meteorological conditions are adopted.

The diagnostic, two-dimensional photochemical model includes specification of the distributions of chemically long-lived species, such as CO, while the densities of short-lived species, such as OH, are calculated assuming photochemical equilibrium. The model thus avoids having to simulate two-dimensional transport. Detailed, two-dimensional photochemical production and destruction rates for species such as CO, CH<sub>4</sub>, O<sub>3</sub>, and NO<sub>x</sub> obtained from this model will be used in formulating atmospheric budgets for these gases, using data gathered by various NASA programs, such as MAPS.

We have begun development of a global model in which coupled box models are used to simulate the various regions of the globe (i.e., North American continent, North Atlantic, Europe, etc). Initially the global box model approach will be used as a diagnostic tool (similar to the diagnostic, two-dimensional model) to determine short-lived species concentrations and for carrying out detailed budget studies. However, when sufficient data are available, transport constants which couple the various box models may be solved for by specifying a variety of observed species distributions and inverting the continuity equations. When this is accomplished, the model will then be capable of analytic studies such as investigations of the response of the system to anthropogenic emissions as a function of time and global region.

TITLE: A MODEL FOR CH<sub>4</sub> AND CO INCORPORATING A TIME-VARYING WIND FIELD AND TROPOPAUSE HEIGHT

P.I. Dr. Leonard K. Peters  
University of Kentucky

STATUS: First year of 2-year continuation proposal approved in FY 1981

# BEST DOCUMENT AVAILABLE

## BRIEF DESCRIPTION OF MODELING:

In the current research, a tropospheric model for the  $\text{CH}_4$ -CO system that considers the physicochemical behavior of these trace gases is being developed. Source-sink descriptions, based on the best available information relative to the major anthropogenic and natural contributions, are incorporated into the model. The distributions of  $\text{CH}_4$  and CO are interrelated by the chemical reactions in which they participate. A chemical kinetic model, using the pseudo-steady-state approximation for the intermediate species (a principal one being OH) and for inclusion in the turbulent transport equations for  $\text{CH}_4$  and CO, accounts for these reactions. The analysis will ultimately model the three-dimensional concentration distributions of  $\text{CH}_4$  and CO in the troposphere.

The model equation has been developed in spherical coordinates with a vertical coordinate system which takes into account the variable topography of the Earth's surface and variable tropopause height. It is being solved using a Galerkin finite element formulation which leads to a system of linear equations for the grid of  $5^\circ$  latitude x  $5^\circ$  longitude, with nine vertical levels from the surface to tropopause.

Model solutions require meteorological data for input and in some studies climatological data have been used to fulfill this requirement. The operational model uses time-varying meteorological data (wind speed and direction, temperature, pressure, relative humidity, etc.) along with source strength data, a chemical reaction mechanism, and a suitable set of initial conditions to predict the  $\text{CH}_4$  and CO concentration distributions in three dimensions within the troposphere. Comparisons of the model with reliable observations, such as those from the MAPS/OFT-2 experiment (Reichle, 1976), will be used to validate and adjust the model.

TITLE: STRATOSPHERIC MODELING

P.I.: Dr. James Hansen  
Goddard Institute for Space Studies

STATUS: Has been supported by Upper Atmosphere Research Program; P.I. now expresses interest in refocusing effort toward tropospheric trace species

## BRIEF DESCRIPTION OF MODELING:

### Background

The atmospheric modeling program at GISS, now in the fifth year, was started with the general objective of developing efficient global models for the purpose of understanding stratospheric/tropospheric processes and their interactions, and to help define observational requirements.

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The approach was to build from a base of experience in radiation with some involvement in GCM modeling. Thus, in the first years the emphasis was on radiation applications (trace gas effects, stratospheric aerosols) together with development of an efficient global 3-D dynamical model. With the latter in hand, emphasis has shifted to global transport studies involving little or no chemistry.

Current staffing provides strong capabilities in radiation (Hansen and Lacis) and in 3-D modeling/dynamics (Rind and Russell). In addition, dynamical analyses and model development have relied heavily on collaboration with Peter Stone (MIT), who has special expertise in dynamical transports and the parameterization of transports.

### *Proposed Refocusing of Effort*

Many of the important global air quality problems require consideration of regional and global transports, as well as chemistry and, in some cases, radiation. Appropriate 3-D modeling capability can help to analyze the sources, sinks and variabilities of different constituents, and seems essential for defining measurement strategies.

We plan to pursue a logical sequence of problems, all of which require treatment of 3-D transport, but with increasing interaction with chemistry, anthropogenic sources, and radiation. It is planned to pursue these problems in collaboration with McElroy (Harvard).

TITLE: CHEMISTRY OF STRATOSPHERIC AND MESOSPHERIC GASES

P.I.: Dr. Michael McElroy  
Harvard University

STATUS: Has been supported by Upper Atmosphere Research Program, also includes tropospheric modeling

### BRIEF DESCRIPTION OF MODELING:

A model for the photochemistry of the global troposphere (Logan et al., 1981) constrained by observed concentrations of  $H_2O$ ,  $O_3$ ,  $CO$ ,  $CH_4$ ,  $NO$ ,  $NO_2$ , and  $HNO_3$  is used. Data for  $NO$  and  $NO_2$  are insufficient to define the global distribution of these gases but are, nonetheless, useful in limiting several of the more uncertain parameters of the model. Concentrations of  $OH$ ,  $HO_2$ ,  $H_2O_2$ ,  $NO$ ,  $NO_2$ ,  $NO_3$ ,  $N_2O_2$ ,  $HNO_2$ ,  $HO_2NO_2$ ,  $CH_3OOH$ ,  $CH_2O$ , and  $CH_3CCL_3$  are calculated as functions of altitude, latitude, and season. The vertical resolution of the model is 2 km except near the ground where computations are carried out at 0, 0.5, 1, and 2 km. The latitudinal resolution is  $15^\circ$  from  $0^\circ$  to  $60^\circ$  latitude. Atmospheric structure (T, P) (U.S. Standard Atmosphere Supplements, 1966) and stratospheric ozone profiles (Hering and Borden, 1967) are specified. The photochemical model is similar to the stratospheric model



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described by Wofsy (1978) and Logan et al. (1978). Results are obtained by solving time-dependent continuity equations. Numerical methods are the same as those of the earlier work.

**TITLE:** THEORETICAL STUDIES OF THE UPPER TROPOSPHERIC AEROSOL LAYER OF THE THE SAHARA DUST

**P.I.:** Dr. Owen B. Toon  
NASA Ames Research Center

**STATUS:** Second year of 3-year proposal approved in FY 1981

## BRIEF DESCRIPTION OF MODELING:

Two complementary models are being constructed which can be united after each one has been thoroughly validated.

### *One-Dimensional Model of Homogeneous and Heterogeneous Chemistry*

This model is based upon our successful models of stratospheric aerosol physics and chemistry. The stratospheric model includes the gas-phase chemistry of the relevant sulfur compounds and a very complete set of physical processes which control the gas-to-particle conversion and the subsequent evolution of the aerosols. The model treats nucleation, coagulation, sedimentation, condensational growth, evaporation, washout, and vertical "eddy" mixing. We have already shown that this model can duplicate in great detail the distributions of both gases and aerosols as measured in the stratosphere. The model has been utilized to study the global cycles of COS and other reduced sulfur compounds, to estimate man's influence on the gaseous and particulate content of the stratosphere, and to analyze data collected under ambient and perturbed conditions.

The major revisions needed to adapt this model to the troposphere involve expansion of gas-phase chemistry and inclusion of aqueous chemical reactions within the drops. Altering the gas-phase chemistry is quite straightforward and has already been accomplished. To this end, we have used our experience with similar stratospheric chemical sets. Our model is unique in that we are able to consider multicomponent aerosols and are therefore able to consider chemical reactions within the droplets in detail. At present our model includes 32 gases and about 90 photochemical reactions involved in the cycles of  $\text{SO}_x$ ,  $\text{CH}_4$ , and CO. We consider aerosols with 40 sizes ranging from 1 nm to about 8  $\mu\text{m}$ . Within a given size category of particles, seven aerosol components are distinguished. In addition to sulfuric acid, we tentatively include ammonium sulfate, ammonium nitrate, silicate, carbon, iron oxides, and sea salt. At present, the sea salt is used as a tracer and Cl chemistry is not considered. We are in the process of incorporating this chemistry in the model and hope to begin simulating the atmosphere late in the summer of 1981.

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## *Three-Dimensional Aerosol Model*

We are constructing a three-dimensional advection model incorporating aerosol physics which will later evolve to become a complete gas- and aerosol-chemistry model. At present, we are concentrating our efforts on transport and on those aerosol microphysical processes which do not involve chemistry. The model is highly flexible. The numerical grid domain can be varied at will, so that different vertical and horizontal resolutions, as well as different aerosol size distribution resolutions, can be used as appropriate. The model may also be switched at will from 1 to 2 to 3 dimensions as needed for a particular problem and as computer power allows. The model is written in sigma coordinates so that variable terrain may be included. Although both aerosols and gases are advected, the model does not predict wind fields. These will be input as a particular problem requires using either observed winds or winds generated from a dynamical model to which we have access (Prof. Anthes, Penn. State).

Presently, the aerosol physics and vertical advection algorithms have been incorporated and validated. We are completing tests of a horizontal advection scheme based on a pseudospectral approach which is highly accurate compared with other advection schemes. We expect the 3-D advection aerosol model to be completed and tested against analytic solutions by early summer of 1981.

TITLE: HYBRID TWO/THREE-DIMENSIONAL PHOTOCHEMICAL MODEL OF THE STRATOSPHERE AND TROPOSPHERE

P.I.: Dr. Louis T. Gidel  
University of Miami

STATUS: One-year task approved in FY 1981 to demonstrate feasibility of approach

### BRIEF DESCRIPTION OF MODELING:

The purpose of the proposed research is to develop and apply a hybrid two three-dimensional photochemical model of the atmosphere as an extension of an existing two-dimensional model in order to make detailed three-dimensional simulations of the chemistry of the troposphere. The model will be aimed especially at explaining the distributions and origins of tropospheric ozone, nitrogen oxides, nitric acid, and carbon monoxide and assessing the relative importance of natural and anthropogenic sources. The proposed work would extend the zonally averaged model of Gidel et al. (1982) and Crutzen and Gidel (1982) to a three-dimensional model in the troposphere for species with photochemical lifetimes less than or on the order of 1 month, while retaining the purely two-dimensional zonally averaged model for all species in the stratosphere and for species in the troposphere that have lifetimes longer than approximately 1 month. The tropospheric three-dimensional part of the model will have decreasing longitudinal resolution with height, starting with 10° longitudinal resolution at the Earth's surface and decreasing stepwise to 360° longitudinal resolution (i.e., zonal averaging) in the lower stratosphere. Such a model can describe the distinctly different chemical

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regimes characteristic of polluted continental and unpolluted marine regions of the free troposphere. It can also provide a framework in which to model the photochemical differences between marine and continental boundary layers and their exchange with the free troposphere, as well as make possible improved parameterizations of rainout processes since marine and continental cloud systems can be distinguished.

## APPENDIX C

POTENTIAL TEMPERATURE AND POTENTIAL VORTICITY

Edwin F. Danielsen

The Earth's atmosphere is a thin, compressible fluid surrounding a large, slightly spheroidal Earth. Its pressure decreases outward radially at the rate of 1 order of magnitude every 15 km, to balance the inward force of gravity. Thus more than 99.9 percent of its mass, including the troposphere and stratosphere, is contained in a spheroidal shell only 50 km in depth and 40,000 km in circumference.

Whether the motions in this shell are turbulent or laminar, as implied by the Greek prefixes tropo- and strato-, depends on the gradients of diabatic heating (radiative and conductive) and on the gradients of potential and kinetic energy stored in the system. Diatomic nitrogen and oxygen, the dominant gases of the mixture, are relatively poor conductors and weak absorbers of visible and infrared radiation. The active gases, triatomic water, carbon dioxide, and ozone, are all minority or trace constituents. Therefore, to a first approximation, we can neglect diabatic processes and their effects on temperature and include only adiabatic processes.

Integration of the first law of thermodynamics between the pressure  $p$  and a reference pressure  $p_0$  ( $p_0 = 1000$  mb, approximately sea-level pressure) defines the potential temperature  $\theta$ :

$$\theta = T \left( \frac{p_0}{p} \right)^k \quad (C1)$$

where  $k = 2/7$  for an ideal diatomic gas and  $T$  is the temperature. When an air parcel ascends in the atmosphere, it expands, and the work done against the environment decreases its internal energy and, therefore, its temperature. Because the pressure deviates only slightly from hydrostatic balance and the gradient is practically vertical, the temperature decreases  $9.8 \text{ K km}^{-1}$ .

Equation (C1) applies strictly to dry air. It can be appropriately and slightly modified for a mixture including water vapor (moist air) but we need not consider these additional complications here. For our purposes, the importance of equation (C1) is that  $\theta$  is conserved for adiabatic processes and quasi-conserved for most diabatic processes in the atmosphere; i.e., it is analogous to the temperature in a liquid.

Also, an important criterion for the occurrence of vertical mixing is the sign of  $\partial\theta/\partial z$ . When  $\partial\theta/\partial z > 0$  an air parcel displaced vertically upward will enter a potentially warmer environment and experience a downward restoring force because it is more dense than the environment (negative buoyancy). Similarly, a parcel displaced downward will become increasingly positive-buoyant and experience an upward restoring force. Conversely, when  $\partial\theta/\partial z < 0$  an upward moving parcel will become



increasingly buoyant and accelerate away from its initial position. One would expect vigorous vertical mixing to occur when  $\partial\theta/\partial z < 0$  and, indeed, it does develop. The result of the mixing is to return  $\partial\theta/\partial z$  to zero.

An excellent example of this type of vertical mixing is the formation and growth of the surface boundary layer as a result of strong surface heating during the day. For reversible processes, the second law of thermodynamics relates the diabatic heating rate  $dq/dt$  per unit mass to changes in  $\theta$ ; i.e.,

$$\frac{dq}{dt} = \frac{C_p T}{\theta} \frac{d\theta}{dt} \quad (C2)$$

where  $C_p$  is the specific heat at constant pressure. Therefore, strong heating adjacent to the surface will reverse the sign of  $\partial\theta/\partial z$  from positive (stable) to negative (unstable).

Many small-scale updrafts will develop and coalesce to form larger and larger updrafts. Compensating downdrafts also develop and vigorous overturning and mixing tends to eliminate the instability, until  $\partial\theta/\partial z \rightarrow 0$  (neutral stability). Trace gases and aerosols emitted from the surface or generated chemically or photochemically near the surface will be mixed simultaneously, leaving their mixing ratio  $X_i$  independent of height. Therefore, in a well mixed boundary layer  $\partial X_i/\partial z$  and  $\partial\theta/\partial z = 0$ , so  $X_i$  will be proportional to  $\theta$  in the layer.

As the boundary layer develops it grows upward by entraining and mixing with air from the "free" troposphere. If the latter contains trace species which were produced earlier in the stratosphere, such as ozone or beryllium 7, these too will be mixed into the boundary layer. In general, surface, tropospheric, and stratospheric sources can all contribute to the final mixing ratios in the boundary layer and direct measurements of horizontal variability in their respective mixing ratios will indicate the relative strengths of the sources.

The above discussion implies that  $\partial\theta/\partial z < 0$  can exist only as a transient state except for air in close proximity to a heat source. Therefore, surface heating and/or upper level cooling will first produce static instability which, in turn, will generate vertical mixing until  $\bar{\theta}$ , the mean value of the mixture, is independent of height. Since  $\partial\theta/\partial z = 0$  corresponds to  $\partial T/\partial z = -9.8 \text{ K km}^{-1}$ , this represents a limiting lapse rate for the troposphere, the "dry adiabatic" lapse rate. The effect of water vapor condensing in updrafts and evaporating in downdrafts is to change  $\partial T/\partial z$  from a constant to a variable with height, the largest reduction occurring at lower elevations where the amount of water changing its phase is largest. Monthly mean soundings from tropical stations have these characteristics. They closely approximate the "moist adiabatic" lapse rate. However, individual soundings have deviations in  $\partial\theta/\partial z$  and  $\partial X/\partial z$  for water vapor, indicating that the mixing is incomplete.

With the exception of well mixed boundary layers, temperature and water vapor profiles at all latitudes indicate that vertical mixing is incomplete throughout the troposphere. However, above the boundary layer other types of mixing must be considered. In particular, conditions in the upper troposphere on the equatorial side of the jet streams occasionally exceed the criterion for inertial instability. This form of instability produces horizontal mixing along surfaces of constant  $\theta$ . It

results from imbalances in the centrifugal forces and the horizontal pressure gradient, just as static instability results from imbalances in the gravitational force and the vertical pressure gradient.

The rotation of the Earth and atmosphere about the polar axis produces centrifugal forces which slightly reduce the force of gravity at the equator, resulting in the Earth's shape adjusting from spherical to a slightly oblate spheroid. When the air moves relative to the Earth, horizontal pressure gradients must develop to balance the so-called Coriolis force, which is equal to the vertical component of the Earth's vorticity times the horizontal windspeed, and is directed to the right of the wind vector.

If this balance is achieved, the wind will experience no relative acceleration and is called a geostrophic wind. If, for the same pressure gradient, the wind is supergeostrophic, inertial forces will rotate it towards the right, towards higher pressure. This will decrease its speed until the pressure force dominates and rotates it back towards its original direction. The result is an inertial oscillation whose period is the same as the vertical component of the Earth's vorticity,  $f = 2 \Omega \sin \phi$ , where  $\Omega$  is the angular speed of the Earth and  $\phi$  is the latitude angle.

The inertial period and restoring force vanishes when the relative vorticity on the constant  $\theta$  surface cancels  $f$ , and inertial instability develops when its magnitude exceeds  $f$ , such that the absolute vorticity is negative in the Northern Hemisphere and positive in the Southern Hemisphere.

Relative vorticity  $\zeta_\theta$  on surfaces of constant  $\theta$  is evaluated by projecting the horizontal wind velocities onto a horizontal surface (a map) and then taking the horizontal cross derivatives:

$$\zeta_\theta = \left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right)_\theta \quad (C3)$$

Thus,  $\partial v / \partial x$  is the change in the meridional velocity with increasing longitude and  $\partial u / \partial y$  is the change in the zonal velocity with increasing latitude, as illustrated in figure C1.

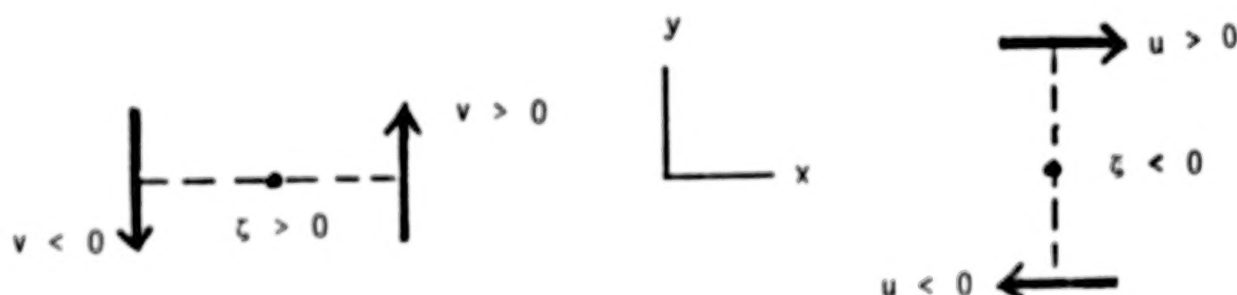


Figure C1. Examples of vorticities due to wind shear.

In the troposphere  $\zeta_\theta$  is usually more negative than  $\zeta_z$  because the surfaces slope upwards towards faster velocities. This condition is illustrated schematically in figure C2, where  $\zeta_z = 0$  and  $\zeta_\theta < 0$ .

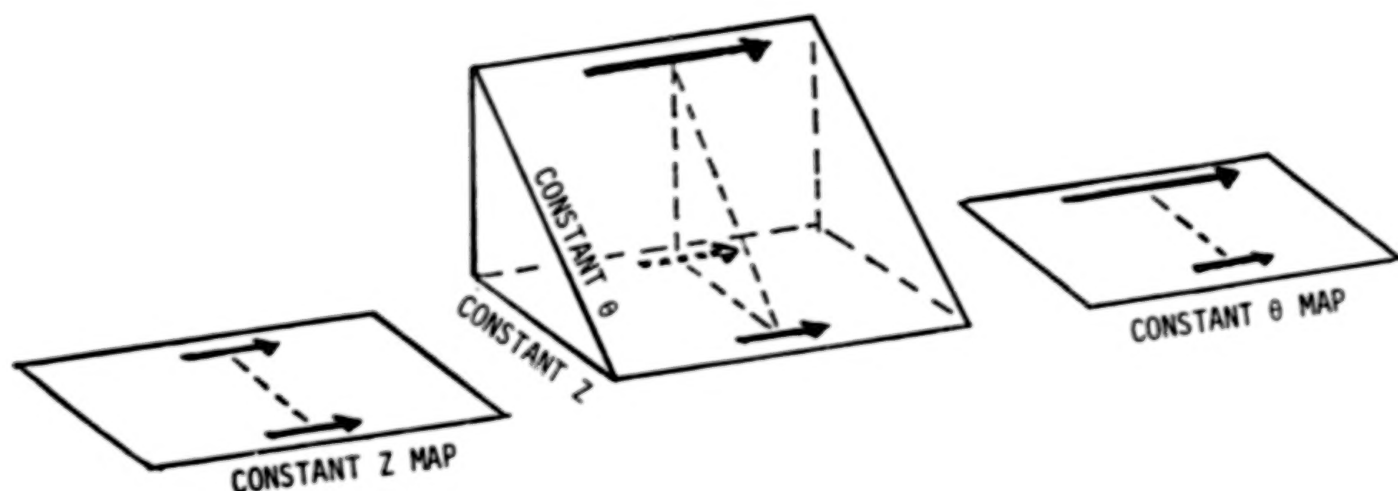


Figure C2. Relationship between  $\zeta_\theta$  and  $\zeta_z$  in the troposphere.

The relationship between  $\zeta_\theta$  and  $\zeta_z$  is expressed by

$$\left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right)_\theta = \left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \right)_z + \frac{\partial v}{\partial z} \frac{\partial z}{\partial x_\theta} - \frac{\partial u}{\partial z} \frac{\partial z}{\partial y_\theta} \quad (C4)$$

where  $\partial z / \partial x_\theta$  and  $\partial z / \partial y_\theta$  are the eastward and northward slopes of the  $\theta$  surface, respectively. In figure C2,  $\zeta_\theta$  is negative because in the last term on the right-hand side both  $\partial u / \partial z$  and  $\partial z / \partial y_\theta$  are positive. Since the slopes of the  $\theta$  surface can be expressed as the negative of the ratio of horizontal to vertical gradients of  $\theta$ ,

$$\frac{\partial \theta}{\partial z} \zeta_\theta = \frac{\partial \theta}{\partial z} \zeta_z + \left( \frac{\partial u}{\partial z} \frac{\partial \theta}{\partial y} - \frac{\partial v}{\partial z} \frac{\partial \theta}{\partial x} \right) \quad (C5)$$

Once again, in figure C2,  $\zeta_\theta < 0$  because  $\partial u / \partial z > 0$  and  $\partial \theta / \partial y < 0$ .

With equation (C5) we have "sneaked up" on the relative component of the potential vorticity, the quasi-conservative quantity of major importance to atmospheric dynamics and to an understanding of the atmospheric variability of trace constituents. Derived by Ertel (1942) and denoted here by  $S$ ,

$$S = \alpha \nabla \theta \cdot [(\nabla \times V) + 2 \Omega] \quad (C6)$$

where  $\alpha$  is the specific volume (reciprocal of the air density),  $\nabla$  is the three-dimensional gradient operator,  $\Omega$  is the angular velocity of the Earth,  $\nabla \times \mathbf{V}$  is the relative vorticity,  $2\Omega$  is the Earth's vorticity, and their sum is the absolute vorticity.

When expanded in the notation used here,

$$S = \alpha \left[ \frac{\partial \theta}{\partial x} \left( \frac{\partial w}{\partial y} - \frac{\partial v}{\partial z} \right)_x + \frac{\partial \theta}{\partial y} \left( \frac{\partial u}{\partial z} - \frac{\partial w}{\partial x} + \lambda \right)_y + \frac{\partial \theta}{\partial z} \left( \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} + f \right)_z \right] \quad (C7)$$

where  $w$  is the vertical velocity, much smaller than  $u$  or  $v$ , and  $\lambda = 2\Omega \cos \phi$ . Products involving the underlined terms are small and can be neglected to an excellent degree of approximation; thus

$$S = \alpha \left( \frac{\partial \theta}{\partial z} \right) (\zeta_\theta + f) \quad (C8)$$

as can be seen by reference to equation (C5) and (C4).

Ertel's potential vorticity theorem, derived from the principles of conservation of mass, momentum, and energy and applicable to a small air parcel, is

$$\frac{dS}{dt} = \alpha (\nabla \times \mathbf{V}) \cdot \nabla \frac{d\theta}{dt} \quad (C9)$$

In general, large values of  $S$  are generated in the upper stratosphere, from 30 to 50 km, as a result of increasing heating with height by the ozone's absorption of solar ultraviolet radiation.

Ozone, beryllium 7, and other trace species generated at these elevations are mixed with the potential vorticity by quasi-horizontal mixing, and their respective mixing ratio's  $\chi_i$ 's become positively correlated with  $S$  (Danielsen, 1968). By a combination of mean circulations and eddy diffusion these quantities are transported down through the extratropical stratosphere and into the troposphere (Danielsen, 1981). Transport to the Earth's surface is completed by a variety of processes, including strong vertical mixing in developing boundary layers, as discussed earlier.

Although neither ozone nor potential vorticity is strictly conserved in its downward transport, the mixing processes are adiabatic and tend to maintain the correlations established aloft. If significant differences in the correlations are discovered by direct measurements, either strong diabatic gradients or photochemical-chemical sources and sinks are responsible. This fact in itself is significant to the atmospheric chemists.

Returning to equation (C9) note that  $S$  is conserved when the processes are adiabatic. In particular,  $S$  is not changed as internal waves propagate through the atmosphere. The reason is implicit in equation (C8). Consider first a stationary wave and flow relative to the wave from west to east, as illustrated in figure C3.



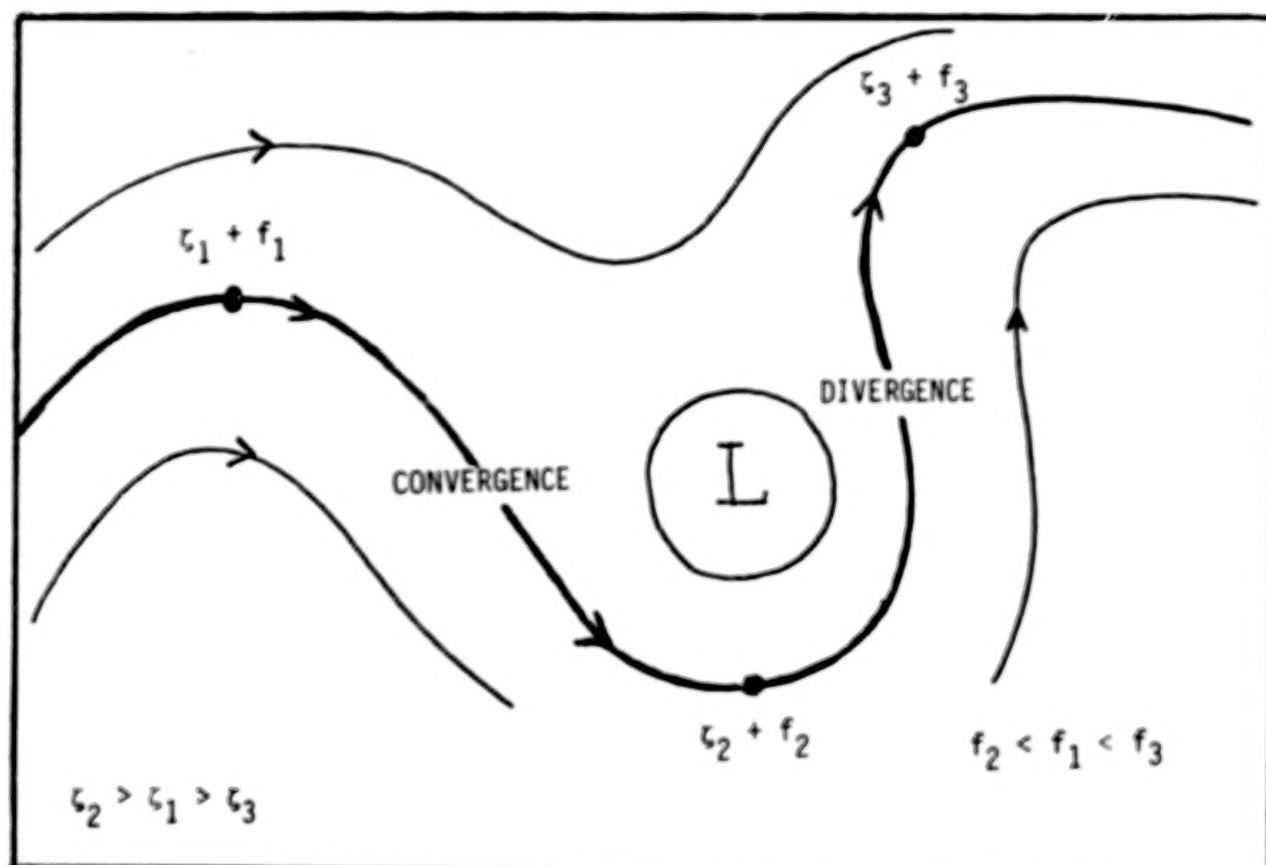


Figure C3. Distribution of convergence and divergence at constant  $\theta$  when wave is quasi-stationary.

As an air parcel moves from the ridge (position 1) to the trough (position 2),  $\zeta_\theta$  will increase and  $f$  will decrease. For the special limiting case of a pure Rossby wave,  $\zeta_\theta + f$  will remain constant, and therefore  $\partial\theta/\partial z$  will remain constant. In general, though, the increase in  $\zeta_\theta$  will substantially exceed the decrease in  $f$ , and convergence at constant  $\theta$  will be required to increase the absolute vorticity of the moving air parcel. The same convergence will simultaneously decrease the static stability  $\partial\theta/\partial z$ . Increasing the absolute vorticity increases inertial stability. Therefore, when waves propagate through the medium or, conversely, the medium moves relative to the wave, static stability is traded for inertial stability, and vice versa.

Both forms of stability are statistically larger in the stratosphere than in the troposphere. The potential vorticity, being proportional to their product, increases more rapidly above the tropopause than does the static stability. By tradition, the conventional criteria for defining the tropopause involve only the static stability. The inertial stability or absolute vorticity is completely ignored. Since it is not conserved, as we have just seen, the identification of air as tropospheric or stratospheric can change as the parcel moves adiabatically. The dependence of the air parcel on its history, still evident in its mixing ratios of trace gases and aerosols, is lost. On the other hand, the history remains intact if the potential vorticity is evaluated because it doesn't change with adiabatic processes.

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Experimental evidence of this important concept was obtained by aircraft measurements of radioactivity during Project Springfield (Danielsen, 1964) and subsequently by measurements of ozone and water vapor (Danielsen and Mohnen, 1977; Danielsen and Hipskind, 1980). These measurements, designed to test the concept of tropopause folding first proposed by Reed (1955) and extended by Reed and Danielsen (1959), were made in tropospheric frontal zones. Mixing ratios of radioactive isotopes of stratospheric origin and ozone were positively correlated with the potential vorticity, while water vapor of tropospheric origin was negatively correlated. The correlations extended from the largest values to the limits of the folded transition zone, indicating that mixing processes maintained the correlations by comparably diluting the mixing ratios of radioactivity and ozone as they reduced the potential vorticity.

As the most conservative atmospheric scalar, whose major source is the upper stratosphere and major sink is the surface, potential vorticity has the potential for developing significantly positive or negative correlations with trace species whose chemical half lives are from  $10^5$  to  $10^8$  seconds, or from several days to several years. On the basis of these correlations the representativeness of individual chemical measurements can be assessed and extrapolated quantitatively to a larger scale context. In addition, the correlations provide an objective criterion for separating that component of the natural variability of a trace constituent which is due to dynamical-transport processes from that which is due to chemical-photochemical processes.

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1. Report No. NASA CP-2235		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle  APPLYING MODELING RESULTS IN DESIGNING A GLOBAL TROPOSPHERIC EXPERIMENT				5. Report Date July 1982	
				6. Performing Organization Code 146-20-10-47	
7. Author(s)				8. Performing Organization Report No. L-15383	
9. Performing Organization Name and Address  NASA Langley Research Center Hampton, VA 23665				10. Work Unit No.	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address  Office of Space Science and Applications National Aeronautics and Space Administration Washington, DC 20546				13. Type of Report and Period Covered  Conference Publication	
				14. Sponsoring Agency Code	
15. Supplementary Notes Working group members: Robert C. Harriss, NASA Langley Research Center (Chairman); Gregory R. Carmichael, Univ. of Iowa; William L. Chameides, Georgia Institute of Technology; Ralph J. Cicerone, National Center for Atmospheric Research; Edwin F. Danielsen, NASA Ames Research Center; Jack Fishman, NASA Langley Research Center; James E. Hansen, Goddard Institute for Space Studies; Ronald J. Lantzy, Exxon Research and Engineering Co.; Donald H. Lenschow, National Center for Atmospheric Research; Shaw C. Liu, National Oceanic and Atmospheric Administration; Jennifer A. Logan, Harvard Univ.; Michael B. McElroy, Harvard Univ.; Leonard K. Peters, Univ. of Kentucky; Richard W. Stewart, NASA Goddard Space Flight Center; Richard S. Stolarski, NASA Goddard Space Flight Center; Owen B. Toon, NASA Ames Research Center.					
16. Abstract This document reports the recommendations of the NASA Working Group on the Application of Modeling Research Results to the Design of a Global Tropospheric Experiment, which met in Virginia Beach, Virginia, July 15-16, 1981. These recommendations evolved through an exchange of written materials both before and after the working group meeting. The objectives of this meeting were to pursue answers to the following questions: (1) What guidance do existing models offer for the design of a global tropospheric field experiment program? More specifically, what priorities should be established for measurement needs in global tropospheric research in the light of current chemical and dynamic understanding? What spatial and temporal scales of importance can be identified for the design of a sampling strategy to obtain data that will improve our understanding of large-scale tropospheric processes? (2) What are the near-term modeling research problems which, if resolved, will enhance the design of a tropospheric air sampling program?					
17. Key Words (Suggested by Author(s))  Troposphere Tropospheric modeling Global tropospheric experiment Tropospheric chemistry				18. Distribution Statement  Unclassified - Unlimited  Subject Category 46	
19. Security Classif. (of this report)  Unclassified		20. Security Classif. (of this page)  Unclassified		21. No. of Pages  94	
				22. Price  A05	